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(54) **Textile treatment.**

(57) The present invention relates to a method of improving the sun protection factor (SPF) of textile fibre material comprising treating the textile fibre material with a composition comprising at least one fluorescent whitening agent which absorbs radiation in the wavelength range 280-400 nm.

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The present invention relates to a method of improving the sun protection factor (SPF) of textile fibre material comprising treating the textile fibre material with a composition comprising at least one fluorescent whitening agent which absorbs radiation in the wavelength range 280-400 nm.

It is known that light radiation of wavelengths 280-400 nm permits tanning of the epidermis. Also known is that rays of wavelengths 280-320 nm (termed UV-B radiation), cause erythemas and skin burning which can inhibit skin tanning.

Radiation of wavelengths 320-400 nm (termed UV-A radiation) is known to induce skin tanning but can also cause skin damage, especially to sensitive skin which is exposed to sunlight for long periods. Examples of such damage include loss of skin elasticity and the appearance of wrinkles, promotion of the onset of erythematous reaction and the inducement of phototoxic or photoallergic reactions.

Any effective protection of the skin from the damaging effects of undue exposure to sunlight clearly needs to include means for absorbing both UV-A and UV-B components of sunlight before they reach the skin surface.

Traditionally, protection of exposed human skin against potential damage by the UV components in sunlight has been effected by directly applying to the skin a preparation containing a UV absorber. In areas of the world, e.g. Australia and America, which enjoy especially sunny climates, there has been a great increase in the awareness of the potential hazards of undue exposure to sunlight, compounded by fears of the consequences of alleged damage to the ozone layer. Some of the more distressing embodiments of skin damage caused by excessive, unprotected exposure to sunlight are development of melanomas or carcinomas on the skin.

One aspect of the desire to increase the level of skin protection against sunlight has been the consideration of additional measures, over and above the direct protection of the skin. For example, consideration has been given to the provision of protection to skin covered by clothing and thus not directly exposed to sunlight.

Most natural and synthetic textile materials are at least partially permeable to UV components of sunlight. Accordingly, the mere wearing of clothing does not necessarily provide skin beneath the clothing with adequate protection against damage by UV radiation. Although clothing containing a deeply coloured dye and/or having a tight weave texture may provide a reasonable level of protection to skin beneath it, such clothing is not practical in hot sunny climates, from the standpoint of the personal comfort of the wearer.

There is a need, therefore, to provide protection against UV radiation for skin which lies underneath clothing, including lightweight summer clothing, which is undyed or dyed only in pale shades. Depending on the nature of the dyestuff, even skin beneath clothing dyed in some dark shades may also require protection from UV radiation.

Such lightweight summer clothing normally has a density of of less than 200 g/m² and has a sun protection factor rating between 1.5 and 20, depending on the type of fibre from which the clothing is manufactured.

The SPF rating of a sun protectant (sun cream or clothing) may be defined as the multiple of the time taken for the average person wearing the sun protectant to suffer sun burning under average exposure to sun. For example, if an average person would normally suffer sun burn after 30 minutes under standard exposure conditions, a sun protectant having an SPF rating of 5 would extend the period of protection from 30 minutes to 2 hours and 30 minutes. For people living in especially sunny climates, where mean sun burn times are minimal, e.g. only 15 minutes for an average fair-skinned person at the hottest time of the day, SPF ratings of at least 20 are desired for lightweight clothing.

Surprisingly, it has now been found that treating a textile fibre material with a composition comprising at least one particular fluorescent whitening agent which can also serve as a UV (ultra-violet) radiation absorber, namely one which absorbs radiation in the wavelength range 280-400 nm, imparts an excellent sun protection factor to the fibre material so treated.

Accordingly, the present invention provides a method of improving the sun protection factor (SPF) of textile fibre material, comprising treating the textile fibre material with a composition comprising at least one fluorescent whitening agent which absorbs radiation in the wavelength range 280-400 nm.

The textile fibre material treated according to the method of the present invention may be composed of a wide variety of natural or synthetic fibres, e.g., wool, polyamide, cotton, polyester, polyacrylic, silk, polypropylene or mixtures thereof, preferably cotton.

The textile fibre material may be in the form of endless filaments (stretched or unstretched), staple fibres, flocks, hanks, textile filament yarns, threads, nonwovens, felts, waddings, flocked structures or woven textile or bonded textile fabrics or knitted fabrics.

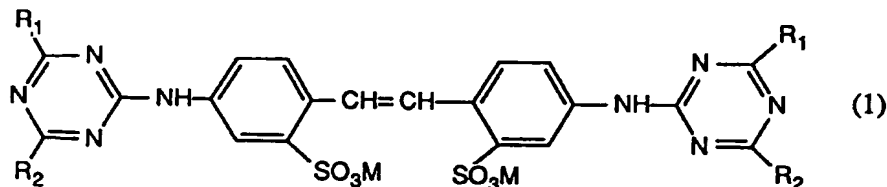
The method according to the present invention may be effected by various techniques. In particular, the method may be conducted by contacting the textile fibre material with one of the following treatment compositions comprising at least one fluorescent whitening agent which absorbs radiation in the wavelength range 280-400 nm.:

- a) an aqueous textile finishing composition;
- b) a detergent composition; or
- c) a post-wash fabric care composition.

The amount of fluorescent whitening agent present in the composition used according to the method of the present invention may vary within a wide range, e.g. from 0.005 to 20 %, based on the weight of the textile fibre material, depending on the particular composition used in the method of the present invention. Thus, when the composition is an aqueous textile finishing composition, the amount of fluorescent whitening agent present in the composition preferably ranges from 0.01 to 3%, especially from 0.05 to 1%, based on the weight of the textile fibre material. When the composition is a detergent composition, the amount of fluorescent whitening agent present in the composition preferably ranges from 0.005 to 2%, especially from 0.01 to 1%, based on the weight of the textile fibre material. When the composition is a post-wash fabric care composition, the amount of fluorescent whitening agent present in the composition preferably ranges from 0.1 to 20%, especially from 1 to 10%, based on the weight of the textile fibre material.

For use from an aqueous textile finishing composition, the fluorescent whitening agent used may be selected from a wide range of chemical types such as 4,4'-bis-(triazinylamino)-stilbene-2,2'-disulfonic acids, 4,4'-bis-(triazol-2-yl)stilbene-2,2'-disulfonic acids, 4,4'-(diphenyl)-stilbenes, 4,4'-distyryl-biphenyls, 4-phenyl-4'-benzoxazolyl-stilbenes, stilbenyl-naphthotriazoles, 4-styryl-stilbenes, bis-(benzoxazol-2-yl) derivatives, bis-(benzimidazol-2-yl) derivatives, coumarines, pyrazolines, naphthalimides, triazinyl-pyrenes, 2-styryl-benzoxazole- or -naphthoxazole derivatives, benzimidazole-benzofuran derivatives or oxanilide derivatives.

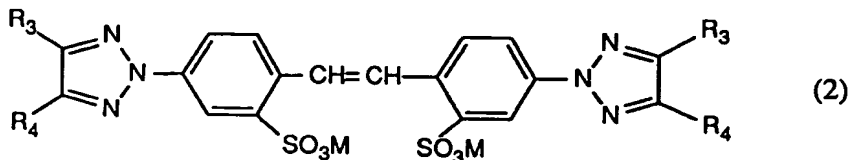
With particular reference to the use of a composition which is an aqueous textile finishing composition, preferred 4,4'-bis-(triazinylamino)-stilbene-2,2'-disulfonic acids are those having the formula:



in which R_1 and R_2 , independently, are phenyl, mono- or disulfonated phenyl, phenylamino, mono- or disulfonated phenylamino, morpholino, $-\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$, $-\text{N}(\text{CH}_3)(\text{CH}_2\text{CH}_2\text{OH})$, $-\text{NH}_2$, $-\text{N}(\text{C}_1\text{-C}_4\text{ alkyl})_2$, $-\text{OCH}_3$, $-\text{Cl}$, $-\text{NH-CH}_2\text{CH}_2\text{SO}_3\text{H}$ or $-\text{NH-CH}_2\text{CH}_2\text{OH}$; and M is H, Na, K, Ca, Mg, ammonium, mono-, di-, tri- or tetra- $\text{C}_1\text{-C}_4\text{-alkylammonium}$, mono-, di- or tri- $\text{C}_1\text{-C}_4\text{-hydroxyalkylammonium}$ or ammonium that is di- or tri-substituted with by a mixture of $\text{C}_1\text{-C}_4\text{-alkyl}$ and $\text{C}_1\text{-C}_4\text{-hydroxyalkyl}$ groups.

Especially preferred compounds of formula (1) are those in which each R_1 is 2,5-disulfophenyl and each R_2 is morpholino; or each R_1 is 2,5-disulfophenyl and each R_2 is $\text{N}(\text{C}_2\text{H}_5)_2$; or each R_1 is 3-sulfophenyl and each R_2 is $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})$ or $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$; or each R_1 is 4-sulfophenyl and each R_2 is $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$; and, in each case, the sulfo group is SO_3M in which M is sodium.

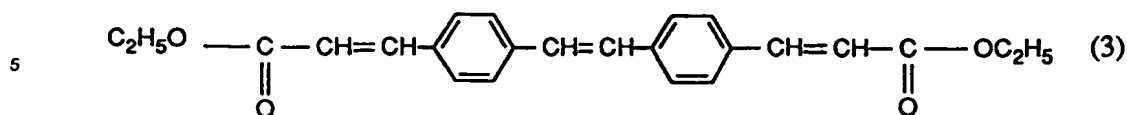
Preferred 4,4'-bis-(triazol-2-yl)stilbene-2,2'-disulfonic acids are those having the formula:



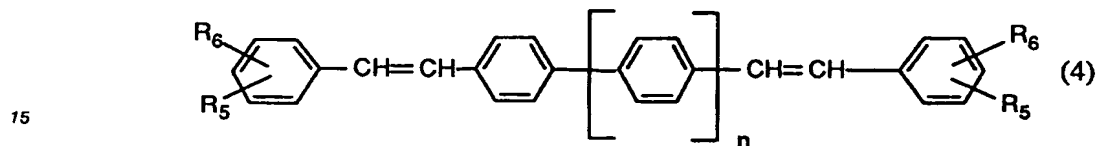
in which R_3 and R_4 , independently, are H, $\text{C}_1\text{-C}_4\text{-alkyl}$, phenyl or monosulfonated phenyl; and M has its previous significance.

Especially preferred compounds of formula (2) are those in which R_3 is phenyl, R_4 is H and M is sodium.

One preferred 4,4'-(diphenyl)-stilbene is that having the formula:



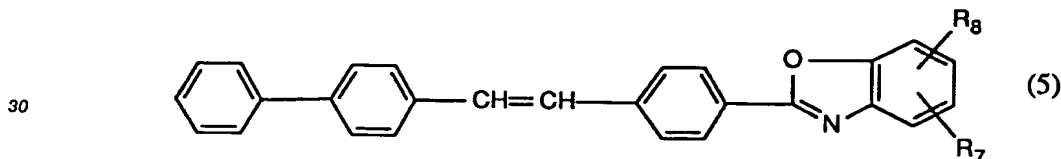
10 Preferably, 4,4'-distyryl-biphenyls used are those of formula:



20 in which R_5 and R_6 , independently, are H, SO_3M , $\text{SO}_2\text{N}(\text{C}_1\text{-C}_4\text{-alkyl})_2$, $\text{O}(\text{C}_1\text{-C}_4\text{-alkyl})$, CN, Cl, $\text{COO}(\text{C}_1\text{-C}_4\text{-alkyl})$, $\text{CON}(\text{C}_1\text{-C}_4\text{-alkyl})_2$ or $\text{O}(\text{CH}_2)_3\text{N}^+\text{(CH}_3)_2\text{An}^-$ in which An^- is an anion of an organic or inorganic acid, in particular a formate, acetate, propionate, glycolate, lactate, acrylate, methanephosphonate, phosphite, dimethyl or diethyl phosphite anion, or a mixture thereof; and n is 0 or 1.

Especially preferred compounds of formula (4) are those in which n is 1 and each R_5 is a 2- SO_3M group in which M is sodium and each R_6 is H, or each R_5 is $\text{O}(\text{CH}_2)_3\text{N}^+\text{(CH}_3)_2\text{An}^-$ in which An^- is acetate.

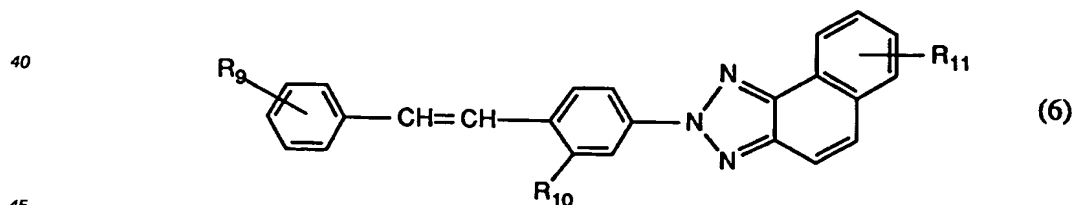
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35 in which R_7 and R_8 , independently, are H, Cl, $\text{C}_1\text{-C}_4\text{-alkyl}$ or $\text{SO}_2\text{-C}_1\text{-C}_4\text{-alkyl}$.

An especially preferred compound of formula (5) is that in which R_7 is 4- CH_3 and R_8 is 2- CH_3 .

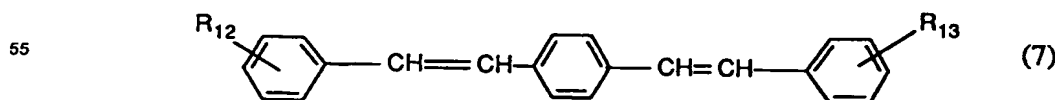
Preferably, stilbenyl-naphthotriazoles used are those of formula:



in which R_9 is H or Cl; R_{10} is SO_3M , $\text{SO}_2\text{N}(\text{C}_1\text{-C}_4\text{-alkyl})_2$, $\text{SO}_2\text{O-phenyl}$ or CN; R_{11} is H or SO_3M ; and M has its previous significance.

50 Especially preferred compounds of formula (6) are those in which R_9 and R_{11} are H and R_{10} is 2- SO_3M in which M is Na.

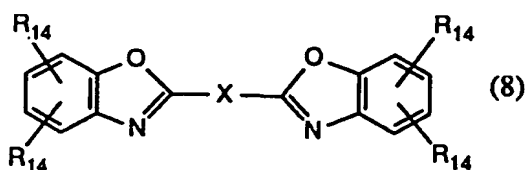
Preferably, 4-styryl-stilbenes used are those of formula:



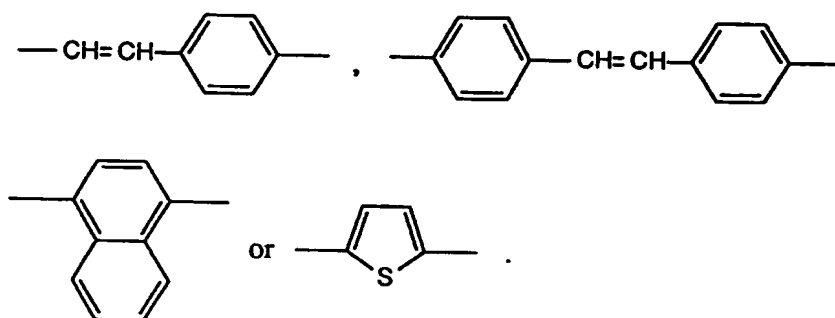
in which R_{12} and R_{13} , independently, are H, SO_3M , $\text{SO}_2\text{N}(\text{C}_1\text{-C}_4\text{-alkyl})_2$, $\text{O}(\text{C}_1\text{-C}_4\text{-alkyl})$, CN, Cl, $\text{COO}(\text{C}_1\text{-C}_4\text{-alkyl})$, $\text{CON}(\text{C}_1\text{-C}_4\text{-alkyl})_2$ or $\text{O}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_2\text{An}^-$ in which An^- is an anion of an organic or inorganic acid, in particular a formate, acetate, propionate, glycolate, lactate, acrylate, methanephosphonate, phosphite, dimethyl or diethyl phosphite anion, or a mixture thereof.

Especially preferred compounds of formula (7) are those in which each of R_{12} and R_{13} is 2-cyano, 2- SO_3M in which M is sodium or $\text{O}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_2\text{An}^-$ in which An^- is acetate.

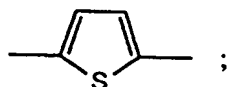
Preferred bis-(benzoxazol-2-yl) derivatives are those of formula:



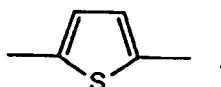
in which R_{14} , independently, is H, $\text{C}(\text{CH}_3)_3$, $\text{C}(\text{CH}_3)_2\text{-phenyl}$, $\text{C}_1\text{-C}_4\text{-alkyl}$ or $\text{COO-C}_1\text{-C}_4\text{-alkyl}$, and X is $-\text{CH}=\text{CH}-$ or a group of formula:



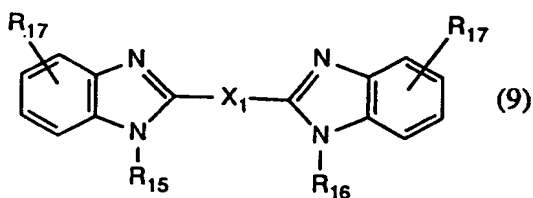
Especially preferred compounds of formula (8) are those in which each R_{14} is H and X is



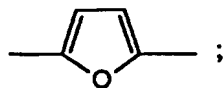
or one group R_{14} in each ring is 2-methyl and the other R_{14} is H and X is $-\text{CH}=\text{CH}-$; or one group R_{14} in each ring is 2- $\text{C}(\text{CH}_3)_3$ and the other R_{14} is H and X is



Preferred bis-(benzimidazol-2-yl) derivatives are those of formula:



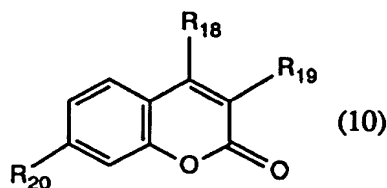
in which R_{15} and R_{16} , independently, are H, C_1 - C_4 -alkyl or CH_2CH_2OH ; R_{17} is H or SO_3M ; X_1 is $-CH=CH-$ or a group of formula:



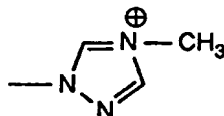
and M has its previous significance.

10 Especially preferred compounds of formula (9) are those in which R_{15} and R_{16} are each H, R_{17} is SO_3M in which M is sodium and X_1 is $-CH=CH-$.

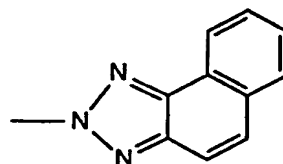
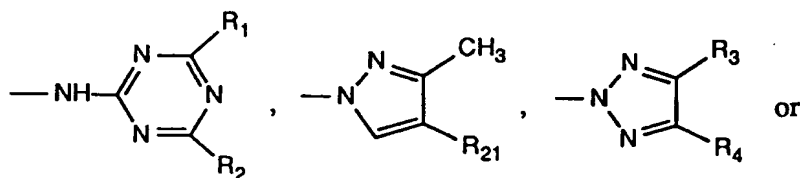
Preferred coumarines are those of formula:



in which R_{18} is H, Cl or CH_2COOH , R_{19} is H, phenyl, $COO-C_1-C_4$ -alkyl or a group of formula:



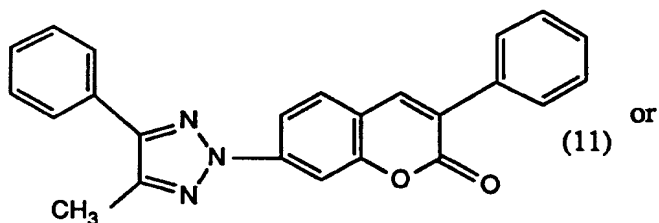
30 and R_{20} is $O-C_1-C_4$ -alkyl, $N(C_1-C_4-alkyl)_2$, $NH-CO-C_1-C_4$ -alkyl or a group of formula:



in which R_1 , R_2 , R_3 and R_4 have their previous significance and R_{21} is H, C_1 - C_4 -alkyl or phenyl.

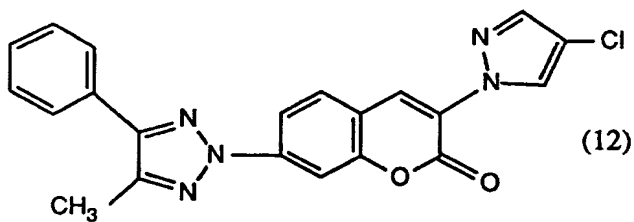
Especially preferred compounds of formula (10) are those having the formula:

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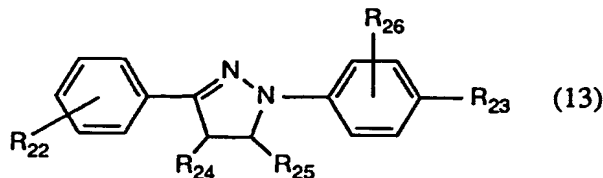
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Preferably, pyrazolines used are those having the formula:

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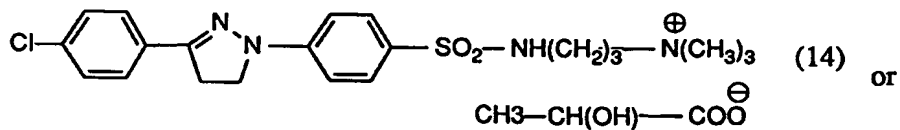
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in which R_{22} is H, Cl or $N(C_1-C_4\text{-alkyl})_2$, R_{23} is H, Cl, SO_3M , SO_2NH_2 , $SO_2NH-(C_1-C_4\text{-alkyl})$, $COO-C_1-C_4\text{-alkyl}$, $SO_2-C_1-C_4\text{-alkyl}$, $SO_2NHCH_2CH_2CH_2N^+(CH_3)_3$ or $SO_2CH_2CH_2CH_2N^+(CH_3)_3$ AN^+ , R_{24} and R_{25} are the same or different and each is H, $C_1-C_4\text{-alkyl}$ or phenyl and R_{26} is H or Cl; and AN^+ and M have their previous significance.

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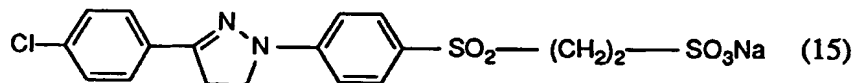
Especially preferred compounds of formula (13) are those in which R_{22} is Cl, R_{23} is $SO_2CH_2CH_2CH_2N^+(CH_3)_3$ AN^+ in which AN^+ is phosphite and R_{24} , R_{25} and R_{26} are each H; or those those having the formula:

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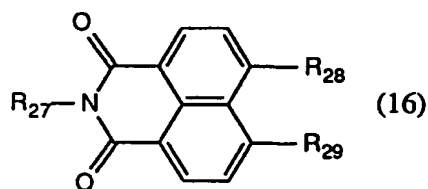
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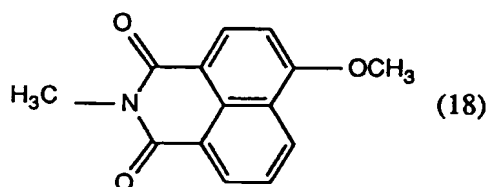
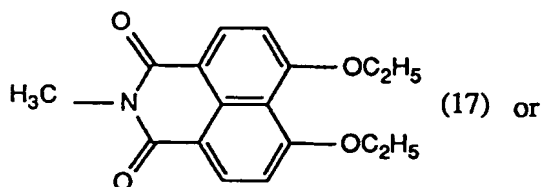
Preferred naphthalimides are those of formula:

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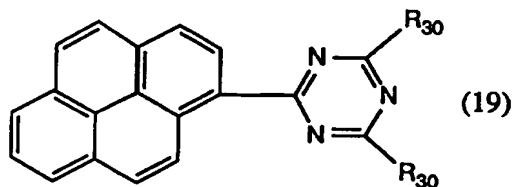


10 in which R₂₇ is C₁-C₄-alkyl or CH₂CH₂CH₂N⁺(CH₃)₃; R₂₈ and R₂₉, independently, are O-C₁-C₄-alkyl, SO₃M or NH-CO-C₁-C₄-alkyl; and M has its previous significance.

Especially preferred compounds of formula (16) are those having the formula:



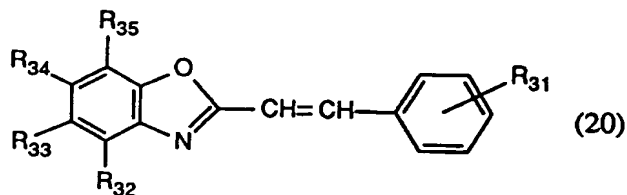
25 Preferred triazinyl-pyrenes used are those of formula:



35 in which each R₃₀, independently, is C₁-C₄-alkoxy.

Especially preferred compounds of formula (19) are those in which each R₃₀ is methoxy.

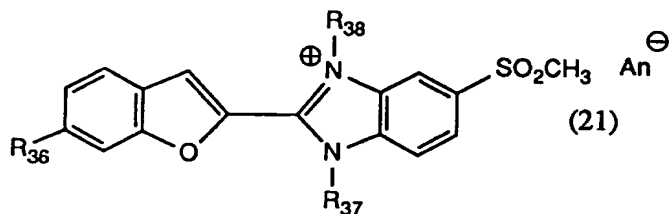
Preferred 2-styryl-benzoxazole- or -naphthoxazole derivatives are those having the formula:



45 in which R₃₁ is CN, Cl, COO-C₁-C₄-alkyl or phenyl; R₃₂ and R₃₃ are the atoms required to form a fused benzene ring or R₃₃ and R₃₅, independently, are H or C₁-C₄-alkyl; and R₃₄ is H, C₁-C₄-alkyl or phenyl.

50 Especially preferred compounds of formula (20) are those in which R₃₁ is a 4-phenyl group and each of R₃₂ to R₃₅ is H.

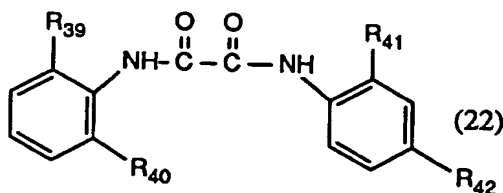
Preferred benzimidazole-benzofuran derivatives are those having the formula:



10 in which R_{36} is C_1 - C_4 -alkoxy; R_{37} and R_{38} , independently, are C_1 - C_4 -alkyl; and An^- has its previous significance.

A particularly preferred compound of formula (21) is that in which R_{36} is methoxy, R_{37} and R_{38} are each methyl and An^- is methane sulfonate.

15 Preferred oxanilide derivatives include those having the formula:

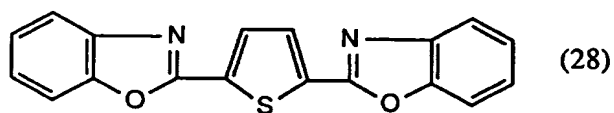
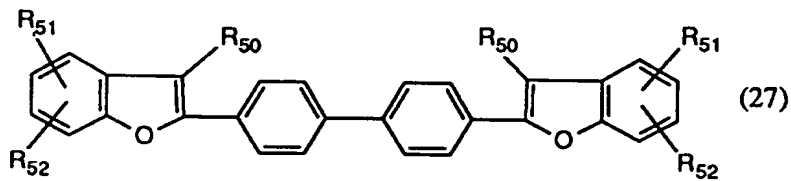
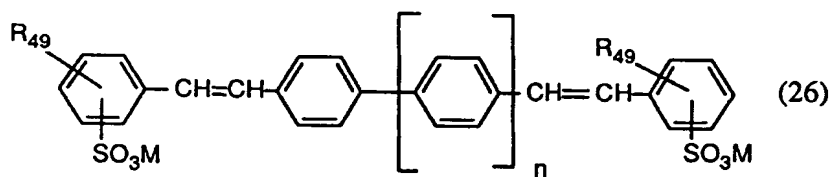
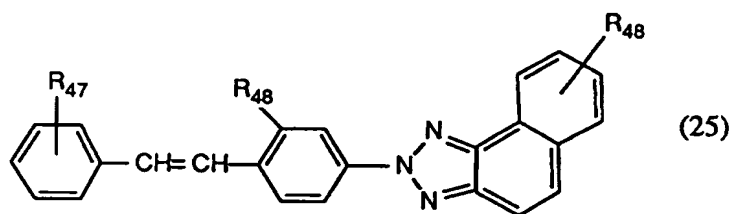
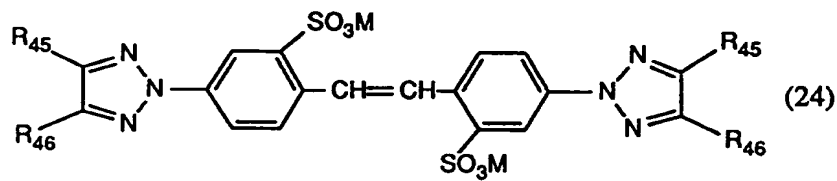
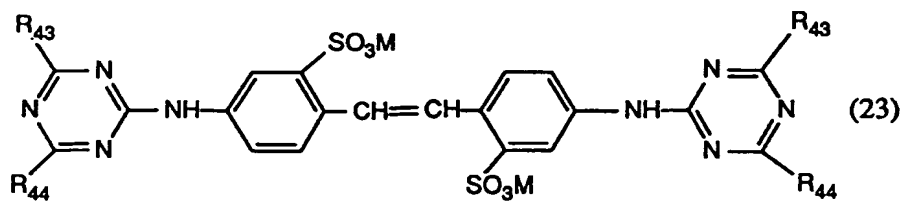


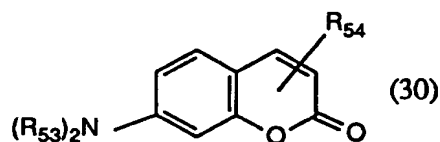
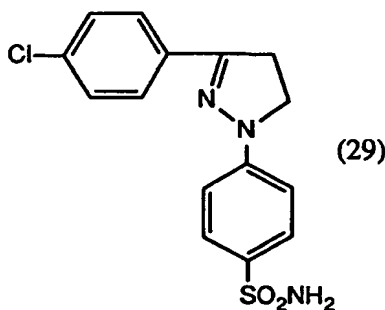
25 in which R_{39} is C_1 - C_4 alkoxy, R_{41} is C_1 - C_4 alkyl, C_1 - C_4 alkyl- SO_3M or C_1 - C_4 alkoxy- SO_3M in which M has its previous significance and R_{40} and R_{42} are the same and each is hydrogen, tert. butyl or SO_3M in which M has its previous significance.

When applied in the present method in a composition which is a textile finishing bath, the fluorescent whitening agent may be used in various formulations such as:

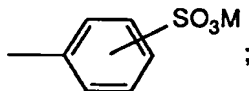
- 30 a) in mixtures with dyes (shading) or pigments, especially white pigments;
 b) in mixtures with carriers, wetting agents, antioxidants, e.g., sterically hindered amines, UV absorbers and/or chemical bleaching agents; or
 c) in admixture with crosslinking or finishing agents (such as starch or synthetic finishes), and in
 35 combination with a wide variety of textile finishing processes, especially synthetic resin finishes, e.g. creaseproof finishes (wash-and-wear, permanent press or non-iron), as well as flameproof finishes, soft handle finishes, antisoiling finishes, antistatic finishes or antimicrobial finishes.

In relation to that aspect of the method of the present invention in which the fluorescent whitening agent is applied to the textile fibre material from a detergent composition, preferred fluorescent whitening agents
 40 for use in the present invention are those having one of the formulae:





20 in which R_{43} and R_{44} , independently, are OH, NH_2 , O-C₁-C₄-alkyl, O-aryl, NH-C₁-C₄-alkyl, N(C₁-C₄-alkyl)₂, N(C₁-C₄-alkyl)(C₁-C₄-hydroxyalkyl), N(C₁-C₄-hydroxyalkyl)₂, NH-aryl, morpholino, S-C₁-C₄-alkyl(aryl), Cl or OH; R_{45} and R_{46} , independently, are H, C₁-C₄-alkyl, phenyl or a group of formula:



30 R_{47} is H, Cl or SO_3M ; R_{48} is CN, SO_3M , S(C₁-C₄-alkyl)₂ or S(aryl)₂; R_{49} is H, SO_3M , O-C₁-C₄-alkyl, CN, Cl, COO-C₁-C₄-alkyl, or CON(C₁-C₄-alkyl)₂; R_{50} is H, C₁-C₄-alkyl, Cl or SO_3M ; R_{51} and R_{52} , independently, are H, C₁-C₄-alkyl, SO_3M , Cl or O-C₁-C₄-alkyl; R_{53} is H or C₁-C₄-alkyl; R_{54} is H, C₁-C₄-alkyl, CN, Cl, COO-C₁-C₄-alkyl, CON(C₁-C₄-alkyl)₂, aryl or O-aryl; and M and n have their previous significance.

In the compounds of formulae (23) to (30), C₁-C₄-alkyl groups are, e.g., methyl, ethyl, n-propyl, isopropyl and n-butyl, especially methyl. Aryl groups are naphthyl or, especially, phenyl.

35 It will be appreciated that the protection afforded to the wearer of the textile material, washed according to this detergent composition aspect of the method of the invention, will last longer when a fluorescent whitening agent is used which has a high lightfastness.

Furthermore, preferred fluorescent whitening agents for use in the present invention have a spectrum covering a relatively low wavelength range, that is exhibiting rather reddish shades. Examples of such fluorescent whitening agents include compounds of formula (23) in which R_{43} and R_{44} are each non-aromatic substituents, such as compounds of formula (23) in which R_{43} and R_{44} , independently, are NH-C₁-C₄-alkyl, O-C₁-C₄-alkyl or morpholino; as well as compounds of formula (26) in which n is 1.

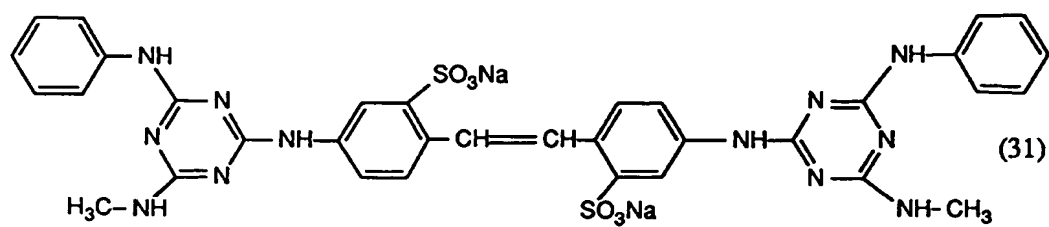
40 Preferred compounds of formula (23) are those in which R_{43} and R_{44} , independently, are O-methyl, O-phenyl, NH_2 , NH-methyl, N(methyl)₂, N(methyl)(hydroxyethyl), NH-ethyl, N(hydroxyethyl)₂, NH-phenyl, S-methyl(phenyl), Cl or OH.

45 Specific examples of preferred compounds of formula (23) are those having the formulae:

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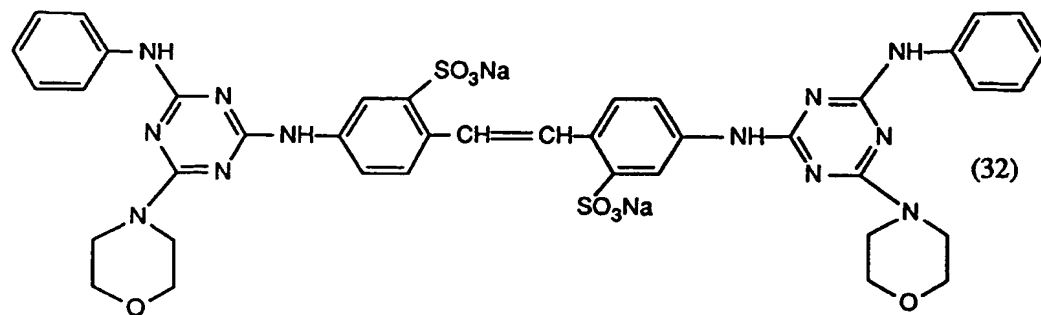
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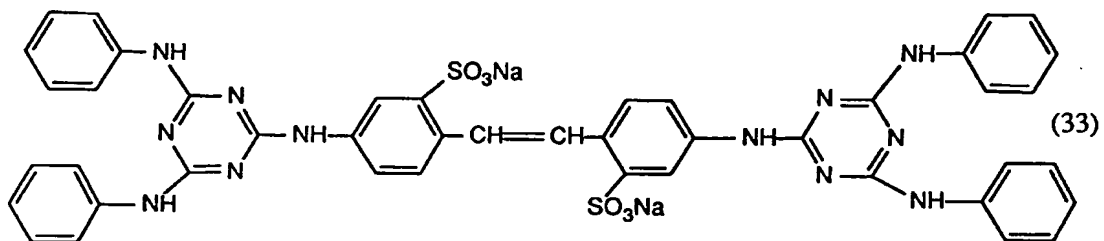
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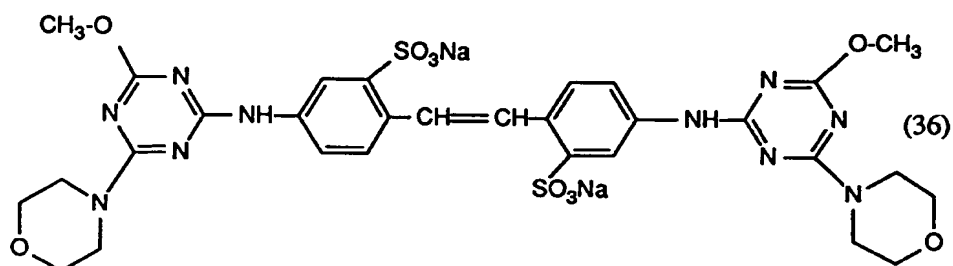
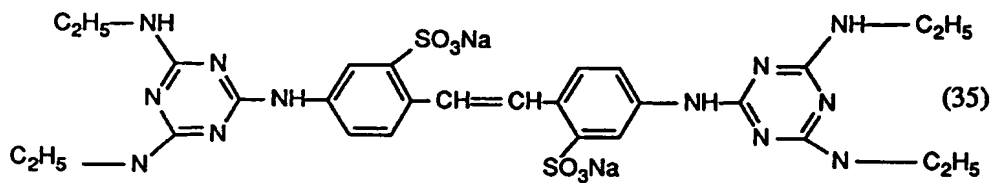
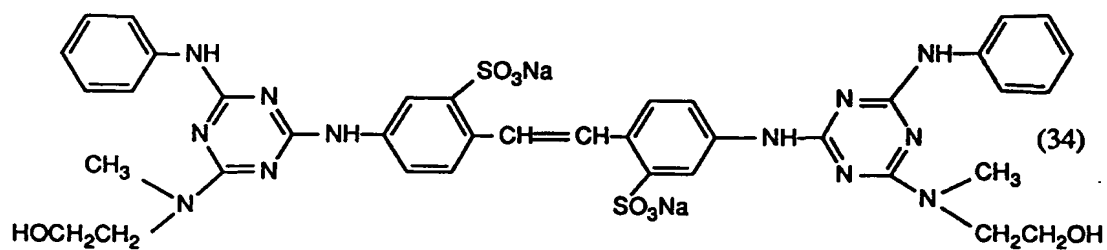
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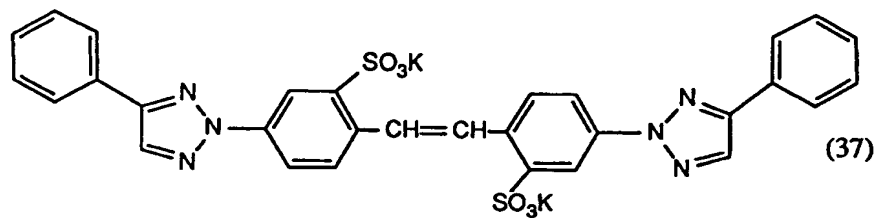
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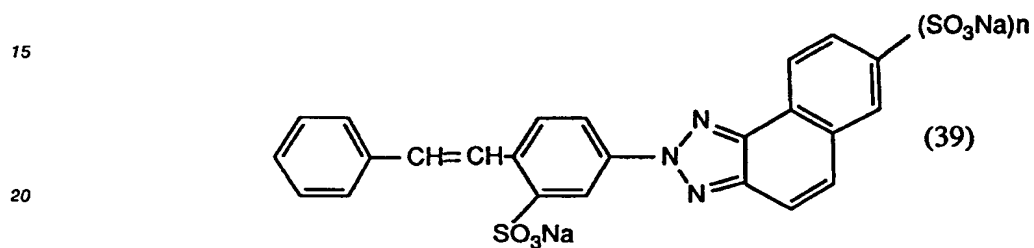
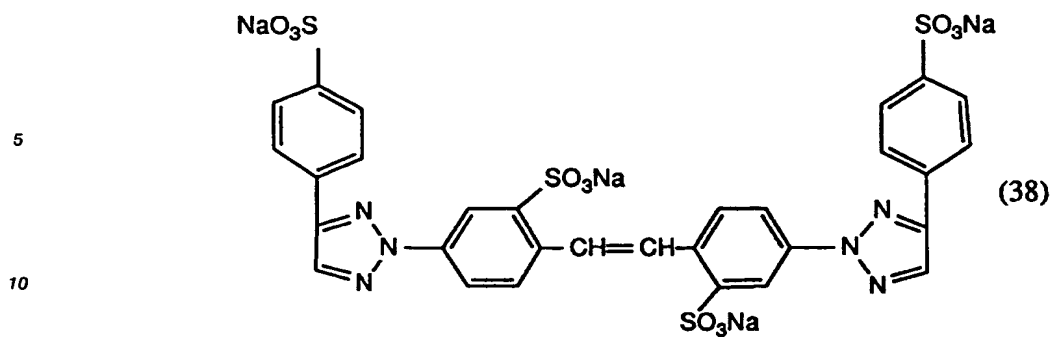
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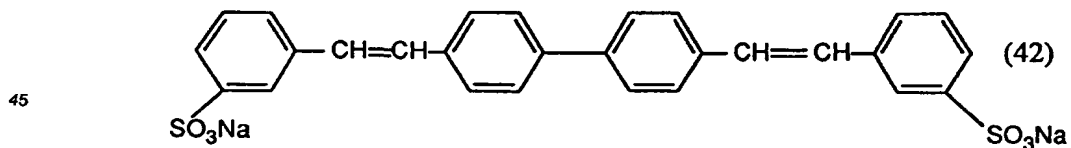
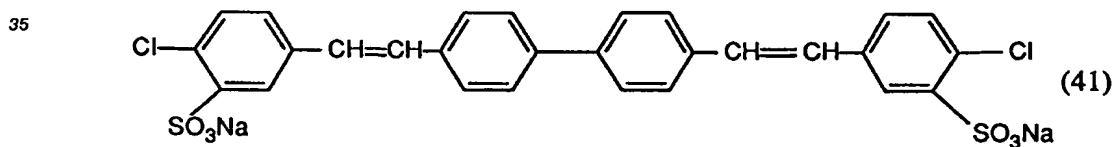
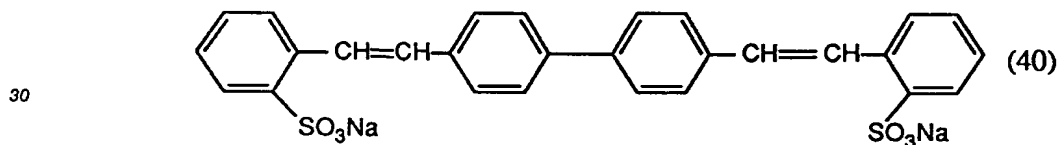
30 Specific preferred examples of compounds of formula (24) are those of formulae:





in which n has its previous significance.

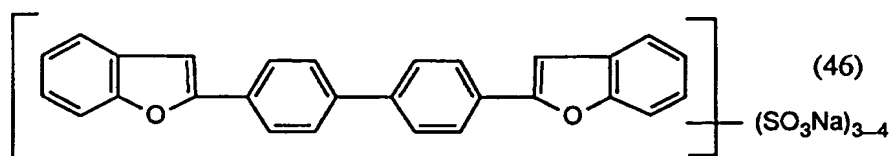
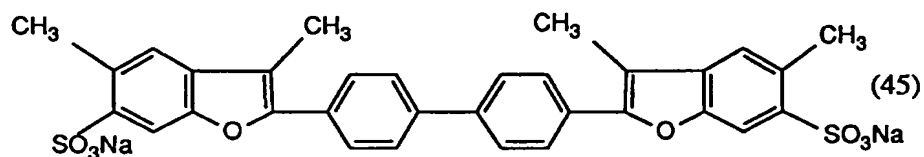
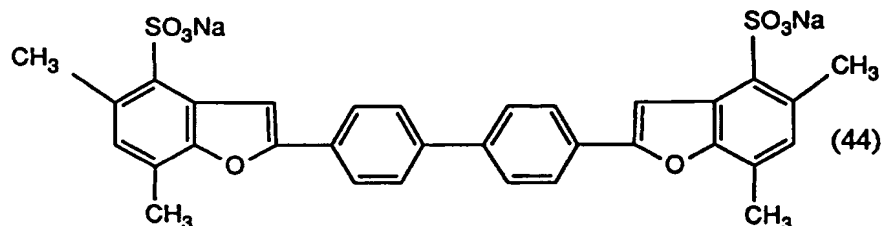
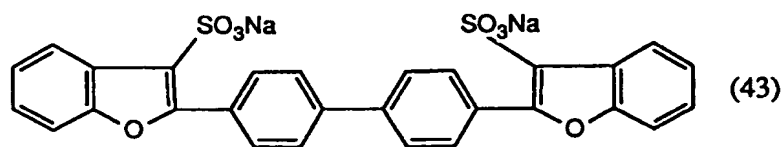
25 Preferred examples of compounds of formula (26) are those having the formulae:



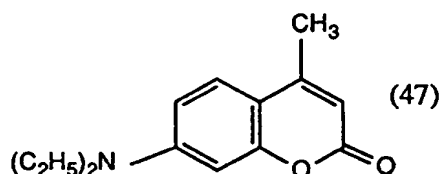
Preferred examples of compounds of formula (27) are those of formulae:

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A preferred example of a compound of formula (30) is that having the formula:

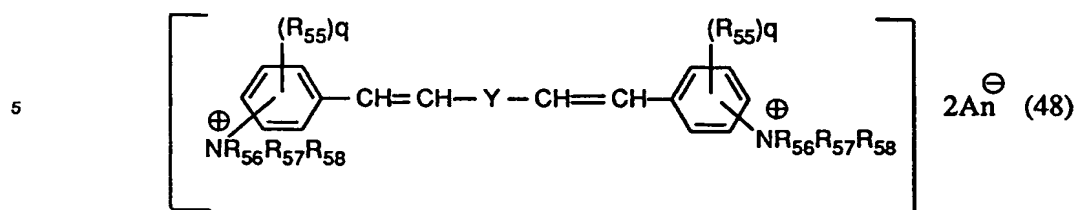


The compounds of formulae (23) to (30) are known and may be obtained by known methods.

In relation to that aspect of the method of the present invention in which the fluorescent whitening agent is applied as a composition comprising a post-wash, rinse cycle fabric care formulation, it is preferred to use a cationic, amphoteric or anionic fluorescent whitening agent. The cationic, amphoteric or anionic fluorescent whitening agent used may be one or more of the wide range of cationic, amphoteric or anionic fluorescent whitening agents, especially those which readily absorb UV light in the range $\lambda = 280-400$ nm and convert the absorbed energy, by a chemical intermediate reaction, into non-interfering, stable compounds or into non-interfering forms of energy. The cationic, amphoteric or anionic fluorescent whitening agent should preferably be compatible with the rinse cycle fabric care agent and should be capable of absorption on to the washed textile material during a rinse cycle fabric care treatment.

The cationic fluorescent whitening agent is preferably of the bistyrylphenyl class or phosphinic acid salt class; the amphoteric fluorescent whitening agent is preferably of the styrene or amine oxide class; and the anionic fluorescent whitening agent is preferably of the aminostilbene, dibenzofuranyl biphenyl or bistyrylphenyl class.

One preferred class of cationic bistyrylphenyl fluorescent whitening agent is that having the formula:



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in which Y is arylene, preferably 1,4-phenylene or 4,4'-diphenylene, each optionally substituted by chloro, methyl or methoxy; q is 1 or 2; R₅₅ is hydrogen, chloro, C₁-C₄-alkyl, C₁-C₄-alkoxy, cyano or C₁-C₄-alkoxycarbonyl; R₅₆ and R₅₇ are C₁-C₄-alkyl, chloroethyl, methoxyethyl, β-ethoxyethyl, β-acetoxyethyl or β-cyanoethyl, benzyl or phenylethyl; R₅₈ is C₁-C₄-alkyl, C₂-C₃-hydroxyalkyl, β-hydroxy-γ-chloropropyl, β-cyanoethyl or C₁-C₄-alkoxy-carbonylethyl; and An[⊖] has its previous significance and is preferably the chloride, bromide, iodide, methosulfate, ethosulfate, benzenesulfonate or p-toluenesulfonate anion when R₅₈ is C₁-C₄-alkyl or An[⊖] is preferably the formate, acetate, propionate or benzoate anion when R₅₈ is β-hydroxy-γ-chloropropyl, β-cyanoethyl or C₁-C₄-alkoxy-carbonylethyl.

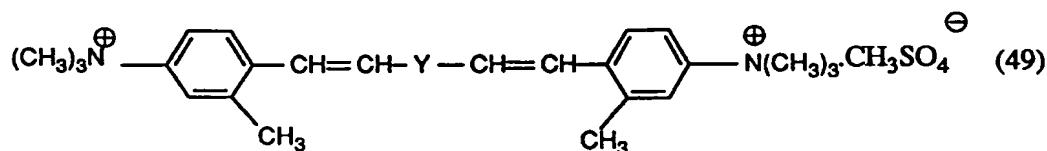
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Preferred compounds of formula (48) are those in which Y is 1,4-phenylene or 4,4'-diphenylene; R₅₅ is hydrogen, methyl or cyano; R₅₆ and R₅₇ are each methyl or cyano; and R₅₈ and An[⊖] have their previously indicated preferred meanings.

20

One particularly preferred compound of formula (48) is that having the formula:

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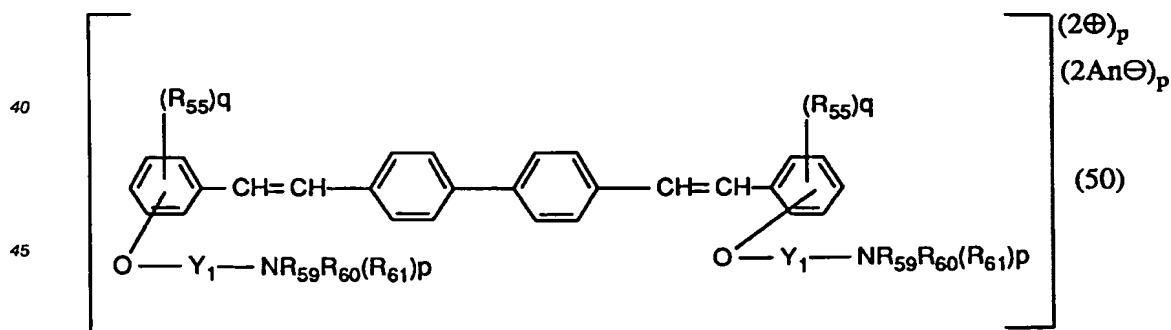


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The compounds of formula (48) and their production are described in US-A-4 009 193.

A further preferred class of cationic bistyrylphenyl fluorescent whitening agent is that having the formula:

35



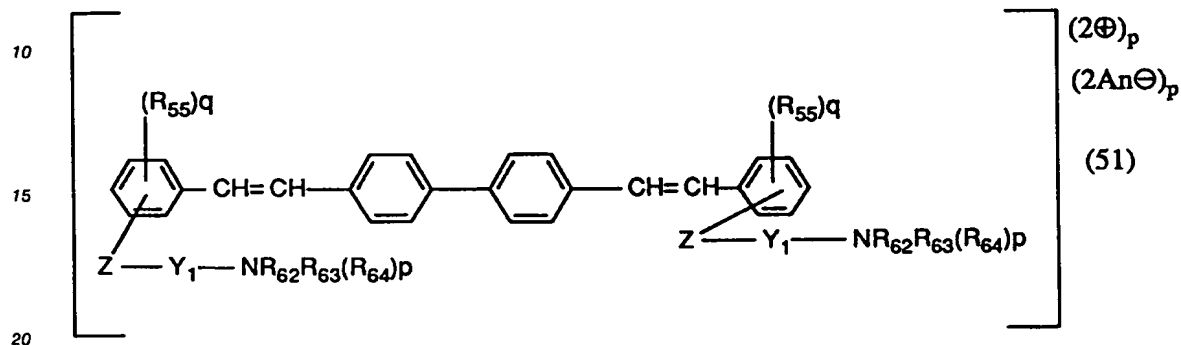
50 in which R₅₅ and q have their previous significance; Y₁ is C₂-C₄-alkylene or hydroxypropylene; R₅₉ is C₁-C₄-alkyl or, together with R₆₀ and the nitrogen to which they are each attached, R₅₉ forms a pyrrolidine, piperidine, hexamethyleneimine or morpholine ring; R₆₀ is C₁-C₄-alkyl or, together with R₅₉ and the nitrogen to which they are each attached, R₆₀ forms a pyrrolidine, piperidine, hexamethyleneimine or morpholine ring; R₆₁ is hydrogen, C₁-C₄-alkyl, C₃-C₄-alkenyl, C₁-C₄-alkoxycarbonylmethyl, benzyl, C₂-C₄-hydroxyalkyl, C₂-C₄-cyanoalkyl or, together with R₅₉ and R₆₀ and the nitrogen atom to which they are each attached, R₆₁ forms a pyrrolidine, piperidine, hexamethyleneimine or morpholine ring; An[⊖] has its previous significance; and p is 0 or 1.

55

Preferred compounds of formula (50) are those in which q is 1; R₅₅ is hydrogen, chlorine, C₁-C₄-alkyl or C₁-C₄-alkoxy; Y₁ is (CH₂)₂; R₅₉ and R₆₀ are the same and each is methyl or ethyl; R₆₁ is methyl or ethyl; p is 1; and AnΘ is CH₃OSO₃ or C₂H₅OSO₃.

The compounds of formula (50) and their production are described in US-A-4 339 393.

A further preferred class of cationic bistyrylphenyl fluorescent whitening agent is that having the formula:

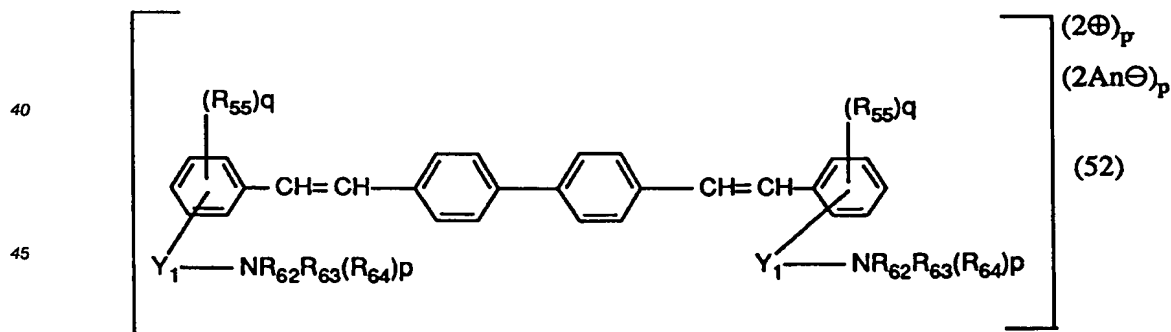


in which R₅₅, Y₁, AnΘ, p and q have their previous significance; R₆₂ and R₆₃, independently, are C₁-C₄-alkyl or C₂-C₃-alkenyl or R₆₂ and R₆₃, together with the nitrogen atom to which they are attached, form a pyrrolidine, piperidine, hexamethyleneimine or morpholine ring; R₆₄ is hydrogen, C₁-C₄-alkyl or C₂-C₃-alkenyl or R₆₂, R₆₃ and R₆₄, together with the nitrogen atom to which they are attached, form a pyridine or picoline ring; and Z is sulfur, -SO₂-, -SO₂NH-, -O-C₁-C₄-alkylene-COO- or -OCO-.

Preferred compounds of formula (51) are those in which R₅₅ is hydrogen, chlorine, C₁-C₄-alkyl or C₁-C₄-alkoxy; R₆₂ and R₆₃, independently, are C₁-C₄-alkyl or, together with the nitrogen atom to which they are attached, form a pyrrolidine, piperidine or morpholine ring; R₆₄ is hydrogen, C₁-C₄-alkyl or C₃-C₄-alkenyl or R₆₂, R₆₃ and R₆₄, together with the nitrogen atom to which they are attached, form a pyridine ring; and Z is sulfur, -SO₂- or -SO₂NH-.

The compounds of formula (51) and their production are described in US-A-4 486 352.

A further preferred class of cationic bistyrylphenyl fluorescent whitening agent is that having the formula:

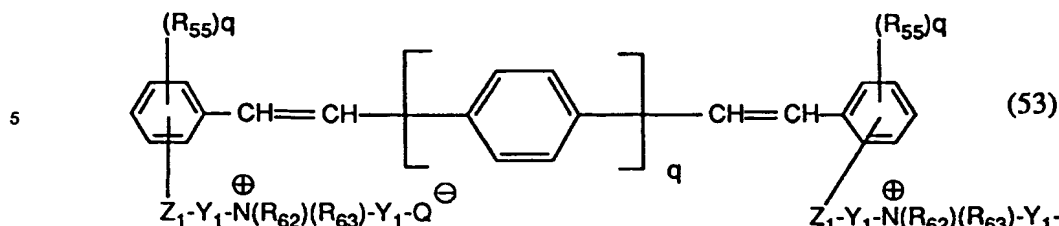


in which R₅₅, R₆₂, R₆₃, R₆₄, Y₁, AnΘ, p and q have their previous significance.

Preferred compounds of formula (52) are those in which q is 1; R₅₅ is hydrogen, chlorine, C₁-C₄-alkyl or C₁-C₄-alkoxy; R₆₂ and R₆₃, independently, are C₁-C₄-alkyl or, together with the nitrogen atom to which they are attached, form a pyrrolidine, piperidine or morpholine ring; R₆₄ is hydrogen, C₁-C₄-alkyl or C₃-C₄-alkenyl or R₆₂, R₆₃ and R₆₄, together with the nitrogen atom to which they are attached, form a pyridine ring.

The compounds of formula (52) and their production are described in US-A-4 602 087.

One preferred class of amphoteric styrene fluorescent whitening agent is that having the formula:



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in which R_{55} , R_{62} , R_{63} , Y_1 and q have their previous significance and Z_1 is oxygen, sulfur, a direct bond, $-\text{COO}-$, $-\text{CON}(R_{65})-$ or $-\text{SO}_2\text{N}(R_{65})-$ in which R_{65} is hydrogen, C_1 - C_4 -alkyl or cyanoethyl; and Q is $-\text{COO}-$ or $-\text{SO}_3$.

15

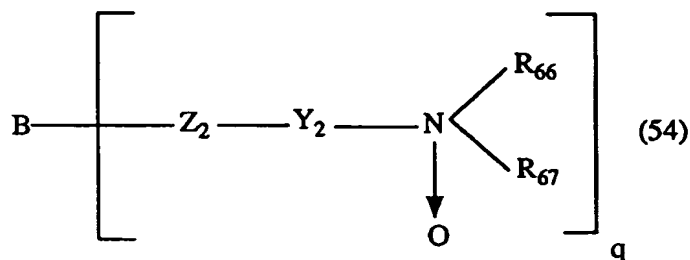
Preferred compounds of formula (53) are those in which Z_1 is oxygen, a direct bond, $-\text{CONH}-$, $-\text{SO}_2\text{NH}-$ or $-\text{COO}-$, especially oxygen; q is 1; R_{62} is hydrogen, C_1 - C_4 -alkyl, methoxy or chlorine; and R_{63} , R_{64} , Y_1 and Q have their previous significance.

The compounds of formula (53) and their production are described in US-A-4 478 598.

One preferred class of amine oxide fluorescent whitening agent is that having the formula:

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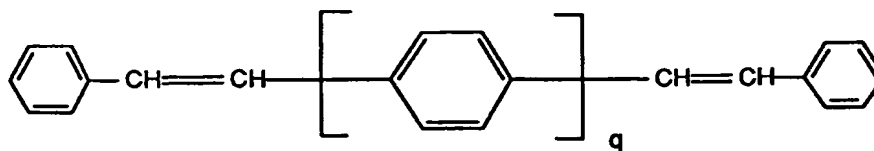
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in which q has its previous significance; B is a brightener radical selected from a 4,4'-distyrylbiphenyl, 4,4'-divinylstilbene, and a 1,4'-distyrylbenzene, each optionally substituted by one to four substituents selected from halogen, C_1 - C_4 -alkyl, C_1 - C_4 -hydroxyalkyl, C_1 - C_4 -halogenoalkyl, C_1 - C_4 -cyanoalkyl, C_1 - C_4 -alkoxy- C_1 - C_4 -alkyl, phenyl- C_1 - C_4 -alkyl, carboxy- C_1 - C_4 -alkyl, carb- C_1 - C_4 -alkoxy- C_1 - C_4 -alkyl, C_1 - C_4 -alkenyl, C_5 - C_8 -cycloalkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -alkenoxyl, C_1 - C_4 -alkoxycarbonyl, carbamoyl, cyano, C_1 - C_4 -alkyl-sulfonyl, phenylsulfonyl, C_1 - C_4 -alkoxysulfonyl, sulfamoyl, hydroxyl, carboxyl, sulfo and trifluoromethyl; Z_2 is a direct bond between B and Y_2 , an oxygen atom, a sulfur atom, $-\text{SO}_2-$, $-\text{SO}_2\text{O}-$, $-\text{COO}-$, $-\text{CON}(R_{68})-$ or $-\text{SO}_2\text{N}(R_{68})-$ in which R_{68} is hydrogen or C_1 - C_4 -alkyl optionally substituted by halogen, cyano, hydroxyl, C_2 - C_5 -carbalkoxy, C_1 - C_4 -alkoxy, phenyl, chlorophenyl, methylphenyl, methoxyphenyl, carbamoyl or sulfamoyl; Y_2 is C_2 - C_4 -alkylene or C_2 - C_4 -alkyleneoxy- C_2 - C_4 -alkylene, each optionally substituted by halogen, hydroxyl, C_2 - C_5 -carbalkoxy, C_1 - C_4 -alkoxy, phenyl, chlorophenyl, methylphenyl, methoxyphenyl, carbamoyl or sulfamoyl; and R_{66} and R_{67} , independently, are C_5 - C_8 -cycloalkyl, C_1 - C_4 -alkyl or phenyl, each optionally substituted by halogen, hydroxyl, C_2 - C_5 -carbalkoxy, C_1 - C_4 -alkoxy, phenyl, chlorophenyl, methylphenyl, methoxyphenyl, carbamoyl or sulfamoyl; in which, in all the carbamoyl or sulfamoyl groups, the nitrogen atom is optionally substituted by one or two C_1 - C_4 -alkyl, C_1 - C_4 -hydroxyalkyl, C_2 - C_5 -cyanoalkyl, C_1 - C_4 -halogenoalkyl, benzyl or phenyl groups.

45

Preferred brightener radicals B are those having the formula:

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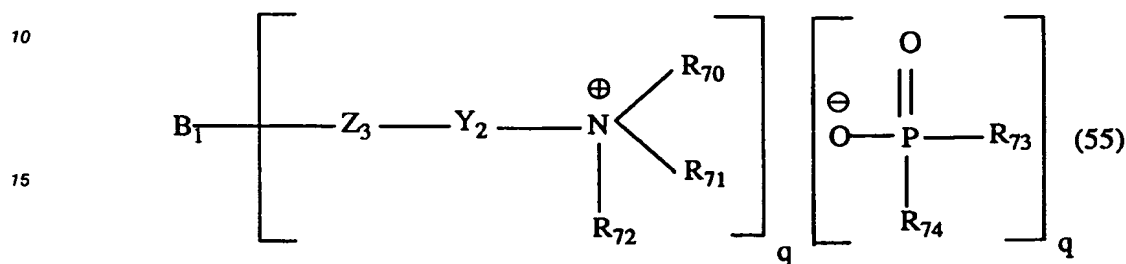
in which q has its previous significance and the rings are optionally substituted as indicated above.

Preferably Z_2 is oxygen, $-\text{SO}_2-$ or $-\text{SO}_2\text{N}(R_{69})-$ in which R_{69} is hydrogen or C_1 - C_4 -alkyl optionally substituted by hydroxyl, halogen or cyano; and R_{66} and R_{67} , independently, are C_1 - C_4 -alkyl optionally

substituted by halogen, cyano, hydroxyl, C₁-C₄-alkoxy, phenyl, chlorophenyl, methylphenyl, methoxyphenyl or C₂-C₅-alkoxycarbonyl. Other preferred compounds of formula (52) are those in which Z₂ is oxygen, sulfur, -SO₂-, -CON(R₆₅)- or -SO₂N(R₆₅)- in which R₆₅ is hydrogen or C₁-C₄-alkyl optionally substituted by hydroxyl, halogen or cyano; and Y₂ is C₁-C₄-alkylene.

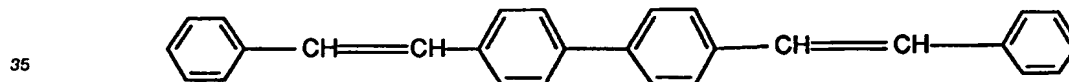
5 The compounds of formula (54) and their production are described in US-A-4 539 161.

One preferred class of cationic phosphinic acid salt fluorescent whitening agent is that having the formula:

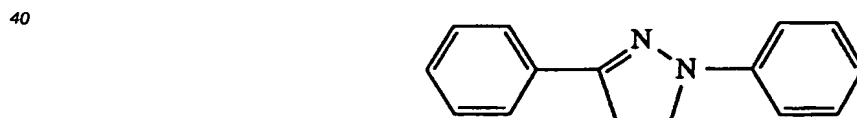


20 in which q and Y₂ have their previous significance; B₁ is brightener radical; Z₃ is a direct bond, -SO₂-C₂-C₄-alkyleneoxy, -SO₂-C₂-C₄-alkylene-COO-, -SO₂-, -COO-, -SO₂-C₂-C₄-alkylene-CON(R₇₅)- or -SO₂N(R₇₅)- in which R₇₅ is hydrogen or C₁-C₄-alkyl optionally substituted by hydroxyl, halogen or cyano; R₇₀ is C₁-C₄-alkyl or C₂-C₄-alkenyl, each optionally substituted by halogen, cyano, hydroxy, C₁-C₄-alkoxycarbonyl or C₁-C₄-alkylcarbonyloxy, or R₇₀ is benzyl, optionally substituted by halogen, C₁-C₄-alkyl or C₁-C₄-alkoxy, or R₇₀, together with R₇₁ or Z₃, forms a pyrrolidine, piperidine or morpholine radical; R₇₁ is C₁-C₄-alkyl or C₂-C₄-alkenyl, each optionally substituted by halogen, cyano, hydroxy, C₁-C₄-alkoxycarbonyl or C₁-C₄-alkylcarbonyloxy, or R₇₁ is benzyl, optionally substituted by halogen, C₁-C₄-alkyl or C₁-C₄-alkoxy, or R₇₁, together with R₇₀, forms a pyrrolidine, piperidine or morpholine radical; R₇₂ is C₁-C₄-alkyl; R₇₃ is hydrogen or C₁-C₄-alkyl, optionally substituted by cyano, hydroxy, C₁-C₄-alkoxycarbonyl or C₁-C₄-alkylcarbonyloxy; and R₇₄ is C₁-C₄-alkyl.

30 Preferably, brightener radical B₁ has the formula:



or the formula:

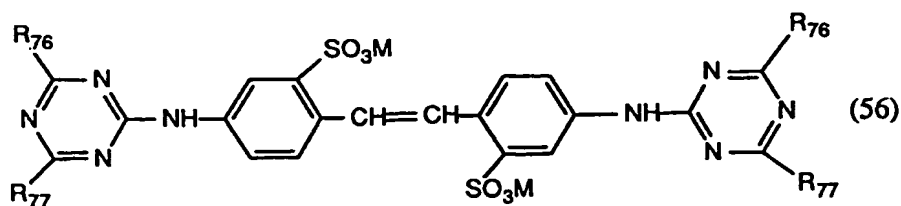


45 each optionally substituted by one to four substituents selected from halogen, C₁-C₄-alkyl, C₁-C₄-hydroxyalkyl, C₁-C₄-halogenoalkyl, C₁-C₄-cyanoalkyl, C₁-C₄-alkoxy-C₁-C₄-alkyl, phenyl-C₁-C₄-alkyl, carboxy-C₁-C₄-alkyl, carb-C₁-C₄-alkoxy-C₁-C₄-alkyl, C₁-C₄-alkenyl, C₅-C₈-cycloalkyl, C₁-C₄-alkoxy, C₁-C₄-alkenoxy, C₁-C₄-alkoxycarbonyl, carbamoyl, cyano, C₁-C₄-alkyl-sulfonyl, phenylsulfonyl, C₁-C₄-alkoxysulfonyl, sulfamoyl, 50 hydroxyl, carboxyl, sulfo and trifluoromethyl.

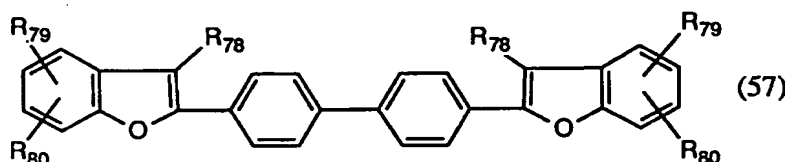
The compounds of formula (55) and their production are described in GB-A-2 023 605.

Preferred bis(triazinyl)diaminostilbene anionic fluorescent whitening agents for use in the present invention are those having the formula:

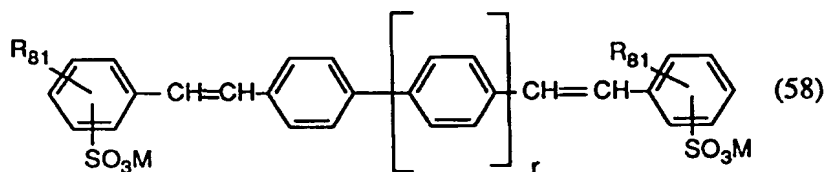
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10 Preferred dibenzofuranyl biphenyl anionic fluorescent whitening agents for use in the present invention are those having the formula:



20 Preferred anionic bistyrylphenyl fluorescent whitening agents for use in the present invention are those having the formula:



30 In the formulae (56) to (58), R_{76} is phenyl optionally substituted by one or two SO_3M groups and R_{77} is $\text{NH-C}_1\text{-C}_4\text{-alkyl}$, $\text{N}(\text{C}_1\text{-C}_4\text{-alkyl})_2$, $\text{NH-C}_1\text{-C}_4\text{-alkoxy}$, $\text{N}(\text{C}_1\text{-C}_4\text{-alkoxy})_2$, $\text{N}(\text{C}_1\text{-C}_4\text{-alkyl})(\text{C}_1\text{-C}_4\text{-hydroxyalkyl})$, $\text{N}(\text{C}_1\text{-C}_4\text{-hydroxyalkyl})_2$; R_{78} is H, $\text{C}_1\text{-C}_4\text{-alkyl}$, CN, Cl or SO_3M ; R_{79} and R_{80} , independently, are H, $\text{C}_1\text{-C}_4\text{-alkyl}$, SO_3M , CN, Cl or $\text{O-C}_1\text{-C}_4\text{-alkyl}$, provided that at least two of R_{78} , R_{79} and R_{80} are SO_3M and the third group has solubilising character; R_{81} is H, SO_3M , $\text{O-C}_1\text{-C}_4\text{-alkyl}$, CN, Cl, $\text{COO-C}_1\text{-C}_4\text{-alkyl}$, or $\text{CON}(\text{C}_1\text{-C}_4\text{-alkyl})_2$; M has its previous significance; and r is 0 or 1.

In the compounds of formulae (56) to (58), $\text{C}_1\text{-C}_4\text{-alkyl}$ groups are, e.g., methyl, ethyl, n-propyl, isopropyl and n-butyl, especially methyl. Aryl groups are naphthyl or, especially, phenyl.

40 Specific examples of preferred compounds of formula (56) are those having the formula (31), (32) or (34), each as hereinbefore defined.

Preferred examples of compounds of formula (57) are those of formula (43), (44), (45) or (46), each as hereinbefore defined.

45 Preferred examples of compounds of formula (58) are those having the formula (40), (41) or (42), each as hereinbefore defined.

The compounds of formulae (56) to (58) are known and may be obtained by known methods.

With respect to that aspect of the method of the present invention in which the fluorescent whitening agent is applied from a textile finishing composition, of particular interest is the co-use of the fluorescent whitening agent with a UV absorber.

50 The UV absorber used may be any of the wide range of known UV absorbers, that is organic compounds which readily absorb UV light, especially in the range $\lambda = 280$ to 400 nm, and which convert the absorbed energy, by a chemical intermediate reaction, into non-interfering, stable compounds or into non-interfering forms of energy. If the textile finishing composition is used in combination with a rinse cycle fabric softener composition, the UV absorber used should, of course, be compatible with the rinse cycle fabric softener composition. In such instances, preferably, the UV absorber used is one which is capable of being absorbed on to the washed textile article during a rinse cycle fabric softener treatment.

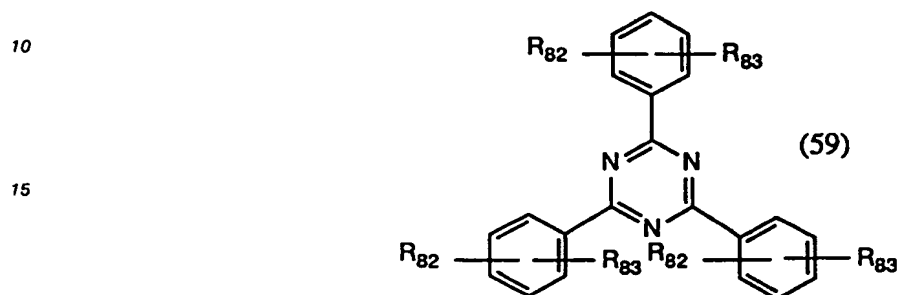
The UV absorber used may be, e.g., an oxalic anilide, an o-hydroxybenzophenone, an o-hydroxyaryl-1,3,5-triazine, a sulphonated-1,3,5-triazine, an o-hydroxyphenylbenzotriazole, a 2-aryl-2H-benzotriazole, a

salicylic acid ester, a substituted acrylonitrile, a substituted arylaminoethylene or a nitrilohydrazone.

Such known UV absorbers for use in the present invention are described, for example, in the US patent specifications 2 777 828, 2 853 521, 3 118 887, 3 259 627, 3 293 247, 3 382 183, 3 403 183, 3 423 360, 4 127 586, 4 141 903, 4 230 867, 4 675 352 and 4 698 064.

5 Preferred UV absorbers for use in the present invention include those of the benzo-triazine or benzo-triazole class.

One preferred class of benzo-triazine UV absorbers is that having the formula:

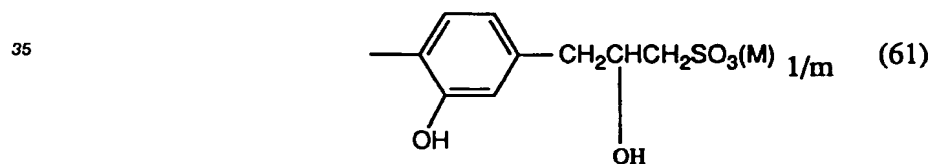


in which R_{82} and R_{83} , independently, are hydrogen, hydroxy or C_1 - C_5 alkoxy.

A second preferred class of triazine UV absorbers is that having the formula:



in which at least one of R_{84} , R_{85} and R_{86} is a radical of formula:

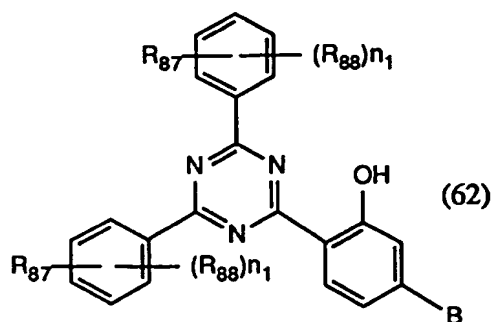


45 in which M has its previous significance; m is 1 or 2; and the remaining substituent(s) R_{84} , R_{85} and R_{86} are, independently, amino, C_1 - C_{12} alkyl, C_1 - C_{12} alkoxy, C_1 - C_{12} alkylthio, mono- or di- C_1 - C_{12} alkylamino, phenyl, phenylthio, anilino or N-phenyl-N- C_1 - C_4 alkylamino, preferably N-phenyl-N-methylamino or N-phenyl-N-ethylamino, the respective phenyl substituents being optionally substituted by C_1 - C_{12} alkyl or -alkoxy, C_5 - C_8 cycloalkyl or halogen.

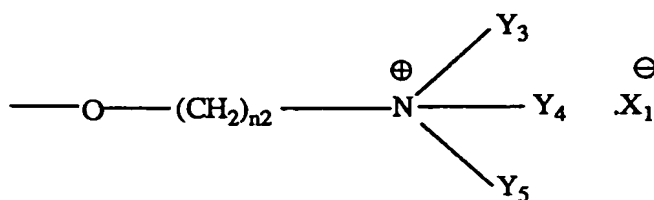
A third preferred class of triazine UV absorbers is that having the formula:

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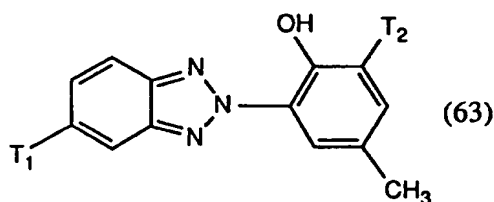


in which R₈₇ is hydrogen or hydroxy; R₈₈, independently, are hydrogen or C₁-C₄alkyl; n₁ is 1 or 2; and B is a group of formula:



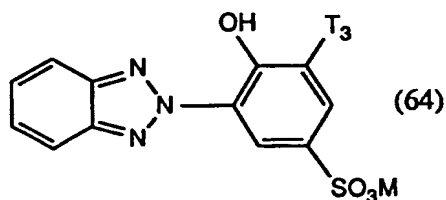
in which n₂ is an integer from 2 to 6 and is preferably 2 or 3; Y₃ and Y₄, independently, are C₁-C₄alkyl optionally substituted by halogen, cyano, hydroxy or C₁-C₄alkoxy or Y₃ and Y₄, together with the nitrogen atom to which they are each attached, form a 5-7 membered heterocyclic ring, preferably a morpholine, pyrrolidine, piperidine or hexamethyleneimine ring; Y₅ is hydrogen, C₃-C₄alkenyl or C₁-C₄alkyl optionally substituted by cyano, hydroxy or C₁-C₄alkoxy or Y₃, Y₄ and Y₅, together with the nitrogen atom to which they are each attached, form a pyridine or picoline ring; and X₁[⊖] is a colourless anion, preferably CH₃OSO₃[⊖] or C₂H₅OSO₃[⊖].

One preferred class of triazole UV absorbers is that having the formula:



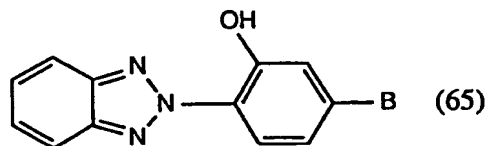
in which T₁ is chlorine or, preferably, hydrogen; and T₂ is a random statistical mixture of at least three isomeric branched sec. C₈-C₃₀, preferably C₈-C₁₆, especially C₉-C₁₂alkyl groups, each having the formula -CH(E₁)(E₂) in which E₁ is a straight chain C₁-C₄alkyl group and E₂ is a straight chain C₄-C₁₅alkyl group, the total number of carbon atoms in E₁ and E₂ being from 7 to 29.

A second preferred class of triazole UV absorbers is that having the formula:



in which M has its previous significance, but is preferably sodium, and T₃ is hydrogen, C₁-C₁₂alkyl or benzyl.

A third preferred class of triazole UV absorbers is that having the formula:



in which B has its previous significance.

In the compounds of formulae (59) to (65), C₁-C₁₂alkyl groups R₈₄, R₈₅, R₈₆ and T₃ may be methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert.-butyl, n-amyl, n-hexyl, n-heptyl, n-octyl, isooctyl, n-nonyl, n-decyl, n-undecyl and n-dodecyl, methyl and ethyl being preferred, except in the case of T₃ for which isobutyl is preferred. C₈-C₃₀alkyl groups T₂ include sec.octyl, decyl, dodecyl, tridecyl, tetradecyl, hexadecyl, octadecyl, eicosyl and triacontyl groups.

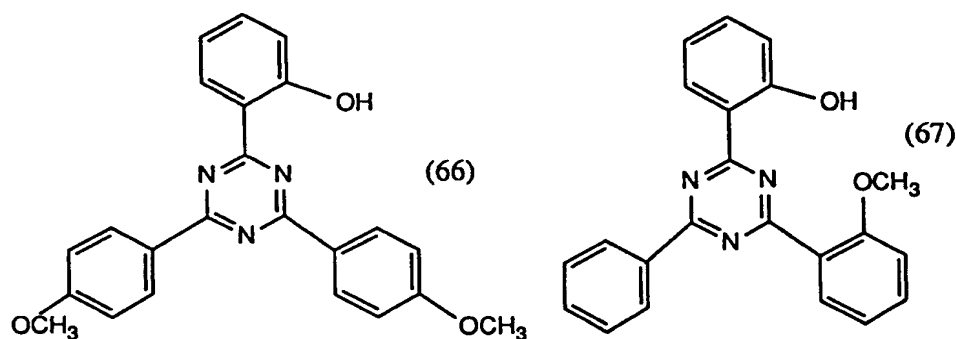
C₁-C₅Alkoxy groups R₈₂ or R₈₃ may be, e.g., methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy, tert.-butoxy or n-amyloxy, preferably methoxy or ethoxy, especially methoxy. C₁-C₁₂Alkoxy groups R₈₄, R₈₅ and R₈₆ include those indicated for the C₁-C₅alkoxy groups R₈₂ or R₈₃ together with, e.g., n-hexoxy, n-heptoxy, n-octoxy, isooctoxy, n-nonyloxy, n-decoxy, n-undecyloxy and n-dodecyloxy, methoxy and ethoxy being preferred.

C₁-C₁₂Alkylthio groups R₈₄, R₈₅ and R₈₆ may be, e.g., methylthio, ethylthio, n-propylthio, isopropylthio, n-butylthio, isobutylthio, tert.-butylthio, n-amylthio, hexylthio, n-heptylthio, n-octylthio, isooctylthio, n-nonylthio, n-decylthio, n-undecylthio and n-dodecylthio, methylthio and ethylthio being preferred.

C₁-C₁₂Mono- or di-alkylamino groups R₈₄, R₈₅ and R₈₆ include, e.g., mono- or di-methylamino, ethylamino, n-propylamino, isopropylamino, n-butylamino, isobutylamino, tert.-butylamino, n-amylamino, n-hexylamino, n-heptylamino, n-octylamino, isooctylamino, n-nonylamino, n-decylamino, n-undecylamino and n-dodecylamino, mono- or di-methylamino or ethylamino being preferred.

The alkyl radicals in the mono-, di-, tri- or tetra-C₁-C₄alkylammonium groups M are preferably methyl. Mono-, di- or tri-C₁-C₄hydroxyalkylammonium groups M are preferably those derived from ethanolamine, di-ethanolamine or tri-ethanolamine. When M is ammonium that is di- or tri-substituted by a mixture of C₁-C₄alkyl and C₁-C₄hydroxyalkyl groups, it is preferably N-methyl-N-ethanolamine or N,N-dimethyl-N-ethanolamine. M is preferably, however, hydrogen or sodium.

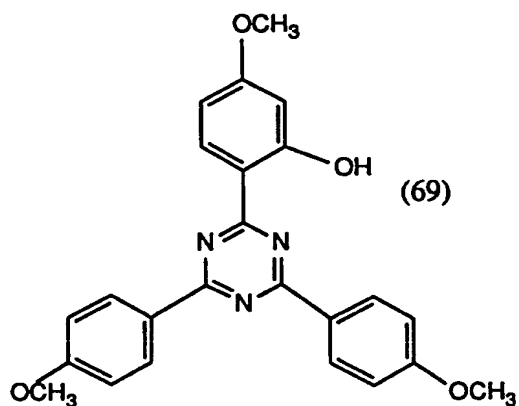
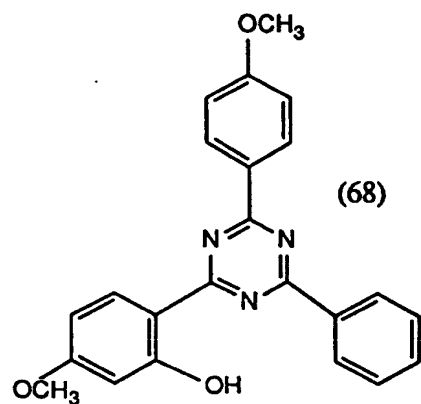
Preferred compounds of formula (59) are those having the formulae:



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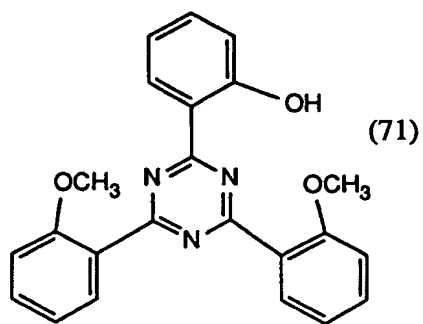
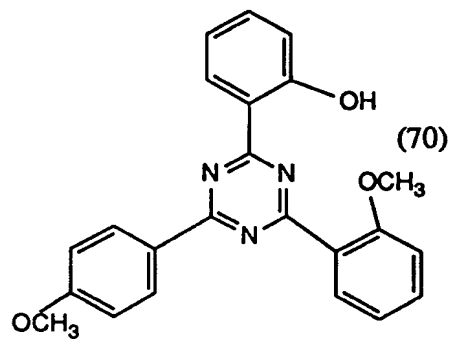
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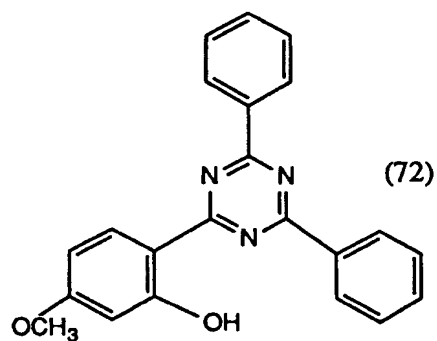
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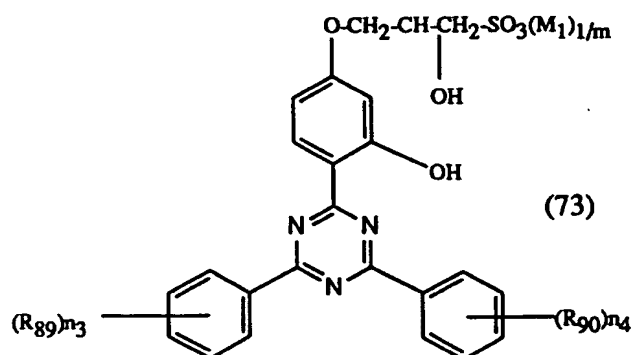


45 The compounds of formula (59) are known and may be prepared e.g. by the method described in U.S. Patent 3 118 887.

Preferred compounds of formula (60) are those having the formula:

50

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15 in which R_{99} and R_{90} , independently, are C_1 - C_{12} alkyl, preferably methyl; m is 1 or 2; M_1 is hydrogen, sodium, potassium, calcium, magnesium, ammonium or tetra- C_1 - C_{12} alkylammonium, preferably hydrogen; and n_3 and n_4 , independently, are 0, 1 or 2, preferably 1 or 2.

Particularly preferred compounds of formula (73) are:

- 20 2,4-diphenyl-6-[2-hydroxy-4-(2-hydroxy-3-sulfopropoxy)-phenyl]-1,3,5-triazine;
 2-phenyl-4,6-bis-[2-hydroxy-4-(2-hydroxy-3-sulfopropoxy)-phenyl]-1,3,5-triazine;
 2,4-bis(2,4-dimethylphenyl)-6-[2-hydroxy-4-(2-hydroxy-3-sulfopropoxy)-phenyl]-1,3,5-triazine; and
 2,4-bis(4-methylphenyl)-6-[2-hydroxy-4-(2-hydroxy-3-sulfopropoxy)-phenyl]-1,3,5-triazine.

The compounds of formula (60) are known and may be prepared in the manner, e.g., described in US Patent 5 197 991.

25 The compounds of formula (63) are known and may be prepared in the manner, e.g., described in US Patent 4 675 352.

The compounds of formula (64) are known and may be prepared in the manner, e.g., described in EP-A-0 314 620.

30 The compounds of formula (65) are known and may be prepared in the manner, e.g., described in EP-A-0 357 545.

The method of the present invention is advantageously conducted in an aqueous medium in which the relevant fluorescent whitening agent is present in solution or as a fine dispersion.

Although most are readily water-soluble, some of the fluorescent whitening agents or UV absorbers for use in the method according to the present invention may be only sparingly soluble in water and may need to be applied in dispersed or emulsified form. For this purpose, they may be milled with an appropriate dispersant, conveniently using quartz balls and an impeller, down to a particle size of 1-2 microns.

As dispersing agents for such sparingly-soluble compounds there may be mentioned:

- acid esters or their salts of alkylene oxide adducts, e.g., acid esters or their salts of a polyadduct of 4 to 40 moles of ethylene oxide with 1 mole of a phenol, or phosphoric acid esters of the adduct of 6 to 30 moles of ethylene oxide with 1 mole of 4-nonylphenol, 1 mole of dinonylphenol or, especially, with 1 mole of compounds which have been produced by the addition of 1 to 3 moles of styrenes on to 1 mole of phenol;
 - polystyrene sulphonates;
 - fatty acid taurides;
 - 45 - alkylated diphenyloxide-mono- or -di-sulphonates;
 - sulphonates of polycarboxylic acid esters;
 - addition products of 1 to 60, preferably 2 to 30 moles of ethylene oxide and/or propylene oxide on to fatty amines, fatty amides, fatty acids or fatty alcohols, each having 8 to 22 carbon atoms, or on to tri- to hexavalent C_3 - C_6 alkanols, the addition products having been converted into an acid ester with an organic dicarboxylic acid or with an inorganic polybasic acid;
 - 50 - lignin sulphonates; and, in particular
 - formaldehyde condensation products, e.g., condensation products of lignin sulphonates and/or phenol and formaldehyde; condensation products of formaldehyde with aromatic sulphonic acids, e.g., condensation products of ditolylethersulphonates and formaldehyde; condensation products of naphthalenesulphonic acid and/or naphthol- or naphthylaminesulphonic acids and formaldehyde; condensation products of phenolsulphonic acids and/or sulphonated dihydroxydiphenylsulphone and phenols or cresols with formaldehyde and/or urea; or condensation products of diphenyloxide-disulphonic acid derivatives with formaldehyde.
- 55

With particular reference to that aspect of the method of the present invention which is effected from a textile finishing composition, and depending on the type of fluorescent whitening agent used, it may be beneficial to carry out the treatment in a neutral, alkaline or acidic bath. The method is usually conducted in the temperature range of from 20 to 140 °C., for example at or near to the boiling point of the aqueous bath, e.g. at about 90 °C.

Solutions of the fluorescent whitening agent, or its emulsions in organic solvents may also be used in the method of the present invention. For example, the so-called solvent dyeing (pad thermofix application) or exhaust dyeing methods in dyeing machines may be used.

In certain cases, the fluorescent whitening agent is made fully effective by an after-treatment. This may comprise a chemical treatment such as treatment with an acid, a thermal treatment or a combined thermal/chemical treatment.

It is often advantageous to use the fluorescent whitening agent in admixture with an assistant or extender such as anhydrous sodium sulfate, sodium sulfate decahydrate, sodium chloride, sodium carbonate, an alkali metal phosphate such as sodium or potassium orthophosphate, sodium or potassium pyrophosphate or sodium or potassium tripolyphosphate, or an alkali metal silicate such as sodium silicate.

The preferred fluorescent whitening agent for use in the method according to the present invention will vary depending on the fibre from which the treated fabric is composed.

Thus, in relation to that aspect of the present invention in which the fluorescent whitening agent is applied from a textile finishing composition, there is preferably used, for the treatment of cotton fabrics, a fluorescent whitening agent of formula (1), (2), (4), (6) or (9) is preferably used; for polyester fabrics, a fluorescent whitening agent of formula (4), (5), (6), (7), (8), (10), (12), (19) or (20) is preferably used; for the treatment of polyamide, a fluorescent whitening agent of formula (1), (2), (4), (5), (6), (7), (8), (10), (11) or (20) is preferably used; for the treatment of polyacrylonitrile, a fluorescent whitening agent of formula (6), (9), (10), (11), (12) or (21) is preferably used; for wool or silk, a fluorescent whitening agent of formula (1), (2), (4), (6), (9), (10) or (11) is preferably used; and for polypropylene, a fluorescent whitening agent of formula (8) is preferably used.

In relation to that aspect of the present invention in which the fluorescent whitening agent is applied from a detergent composition, the use according to the present invention is preferably effected by washing the textile fibre material at least once with the detergent composition, preferably at a temperature ranging from 10 to 100 °C., especially from 15 to 60 °C.

The detergent composition used preferably comprises:

- i) 5-90%, preferably 5-70% of an anionic surfactant and/or a nonionic surfactant;
- ii) 5-70%, preferably 5-40% of a builder;
- iii) 0-30%, preferably 1-12% of a peroxide;
- iv) 0-10%, preferably 1-6% of a peroxide activator and/or 0-1%, preferably 0.1-3% of a bleaching catalyst;
- v) 0.005-2%, preferably 0.01-1% of at least one fluorescent whitening agent which absorbs radiation in the wavelength range 280-400 nm; and
- vi) 0.005-10%, preferably 0.1-5% of one or more auxiliaries, each by weight, based on the total weight of the detergent.

The detergent may be formulated as a solid, as an aqueous liquid comprising 5-50, preferably 10-35% water or as a non-aqueous liquid detergent, containing not more than 5, preferably 0-1 wt.% of water, and based on a suspension of a builder in a non-ionic surfactant, as described, e.g., in GB-A-2158454.

The anionic surfactant component may be, e.g., a sulphate, sulphonate or carboxylate surfactant, or a mixture of these.

Preferred sulphates are alkyl sulphates having 12-22 carbon atoms in the alkyl radical, optionally in combination with alkyl ethoxy sulphates having 10-20 carbon atoms in the alkyl radical.

Preferred sulphonates include alkyl benzene sulphonates having 9-15 carbon atoms in the alkyl radical.

In each case, the cation is preferably an alkali metal, especially sodium.

Preferred carboxylates are alkali metal sarcosinates of formula $R-CO(R')CH_2COOM^1$ in which R is alkyl or arkenyl having 9-17 carbon atoms in the alkyl or alkenyl radical, R' is C₁-C₄ alkyl and M¹ is alkali metal.

The nonionic surfactant component may be, e.g., a condensate of ethylene oxide with a C₃-C₁₅ primary alcohol having 3-8 moles of ethylene oxide per mole.

The builder component may be an alkali metal phosphate, especially a tripolyphosphate; a carbonate or bicarbonate, especially the sodium salts thereof; a silicate; an aluminosilicate; a polycarboxylate; a polycarboxylic acid; an organic phosphonate; or an aminoalkylene poly (alkylene phosphonate); or a mixture of these.

Preferred silicates are crystalline layered sodium silicates of the formula $\text{NaHSi}_m\text{O}_{2m+1} \cdot p\text{H}_2\text{O}$ or $\text{Na}_2\text{Si}_m\text{O}_{2m+1} \cdot p\text{H}_2\text{O}$ in which m is a number from 1.9 to 4 and p is 0 to 20.

Preferred aluminosilicates are the commercially-available synthetic materials designated as Zeolites A, B, X, and HS, or mixtures of these. Zeolite A is preferred.

5 Preferred polycarboxylates include hydroxypolycarboxylates, in particular citrates, polyacrylates and their copolymers with maleic anhydride.

Preferred polycarboxylic acids include nitrilotriacetic acid and ethylene diamine tetra-acetic acid.

Preferred organic phosphonates or aminoalkylene poly (alkylene phosphonates) are alkali metal ethane 1-hydroxy diphosphonates, nitrilo trimethylene phosphonates, ethylene diamine tetra methylene
10 phosphonates and diethylene triamine penta methylene phosphonates.

Any peroxide component may be any organic or inorganic peroxide compound, described in the literature or available on the market, which bleaches textiles at conventional washing temperatures, e.g. temperatures in the range of from 5°C. to 90°C. In particular, the organic peroxides are, for example, monoperoxides or polyperoxides having alkyl chains of at least 3, preferably 6 to 20, carbon atoms; in
15 particular diperoxydicarboxylates having 6 to 12 C atoms, such as diperoxyperazates, diperoxypersebacates, diperoxyphthalates and/or diperoxydodecanedioates, especially their corresponding free acids, are of interest. It is preferred, however, to employ very active inorganic peroxides, such as persulphate, perborate and/or percarbonate. It is, of course, also possible to employ mixtures of organic and/or inorganic peroxides. The peroxides, especially the inorganic peroxides, are preferably activated by the inclusion of a
20 activator such as tetraacetyl ethylenediamine or nonoxyloxybenzene sulfonate. Bleaching catalysts which may be added include, e.g., enzymatic peroxide precursors and/or metal complexes. Preferred metal complexes are manganese or iron complexes such as manganese or iron phthalocyanines or the complexes described in EP-A-0 509 787.

The detergents used will usually contain one or more auxiliaries such as soil suspending agents, for
25 example sodium carboxymethylcellulose; salts for adjusting the pH, for example alkali or alkaline earth metal silicates; foam regulators, for example soap; salts for adjusting the spray drying and granulating properties, for example sodium sulphate; perfumes; and also, if appropriate, antistatic and softening agents; such as smectite clays; enzymes, such as amylases; photobleaching agents; pigments; and/or shading agents. These constituents should, of course, be stable to any bleaching system employed.

30 The preferred fluorescent whitening agent for use in the detergent used according to the present invention will vary depending on the fibre from which the treated fabric is composed.

Thus, for the treatment of polyester fabrics from a detergent composition, a fluorescent whitening agent of formula (28) is preferably used. For the treatment of polyamide, a fluorescent whitening agent of formula (29), (30) or (34) is preferably used. For wool, a fluorescent whitening agent of formula (29), (30) or (37) is
35 preferably used

Relative to the use of a conventional UV absorber, the use in the present invention of a fluorescent whitening agent which absorbs radiation in the wavelength range 280-400 nm from a detergent composition has the following advantages: easier application since it exhausts on to the fibre; coloured textile goods can be washed with a detergent composition according to the claimed use (previously it was generally believed
40 that FWAs had no useful role to play in detergents for coloured goods - see, e.g., A.E.Lee "Technology developments in laundry products", Proc. of the 3rd World Conference on Detergents, Montreux, Sept. 1994, AOCs Press, p.73, § "Color variants"); the UV protection is regularly renewed on washing; yellowing of the textile material caused by o-hydroxy groups in the UV absorber is avoided; minor amounts of the fluorescent whitening agent provide very high extinction values; the textile material is more wash resistant;
45 and higher SPF values are attainable.

With respect to that aspect of the method of the present invention in which the fluorescent whitening agent is applied to the textile fibre material via a post-wash fabric care composition, the present invention provides, as a further aspect, a stable, concentrated fabric care composition comprising 0.3 to 10, preferably 0.3 to 3% by weight of a fluorescent whitening agent which is compatible with a fabric care
50 ingredient, preferably a cationic, amphoteric or anionic fluorescent whitening agent, based on the total weight of the composition, and a fabric care ingredient, preferably a fabric softener, a stain release or stain repellent ingredient or a water-proofing agent, the remainder being substantially water.

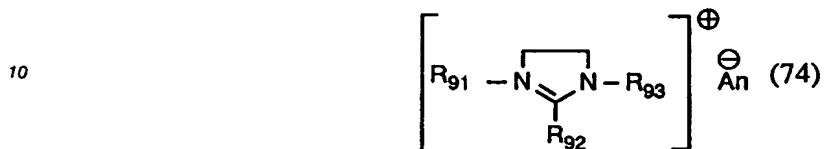
The fabric care ingredient is preferably present in an amount of from 2 to 25, preferably 5 to 20% by weight, based on the total weight of the composition.

55 The present invention provides, as a still further aspect, a stable, concentrated rinse cycle fabric softener composition comprising 2 to 25, preferably 5 to 20% by weight of a fabric softening agent, preferably a cationic fabric softening agent and 0.3 to 10, preferably 0.3 to 3% by weight of a fluorescent whitening agent which is compatible with the fabric softening agent, preferably a cationic, amphoteric or

anionic fluorescent whitening agent, each based on the total weight of the composition, the remainder being substantially water.

Preferred examples of cationic fabric softening agents include imidazolines, quaternary ammonium compounds, ester amide amine salts, as well as mixtures thereof.

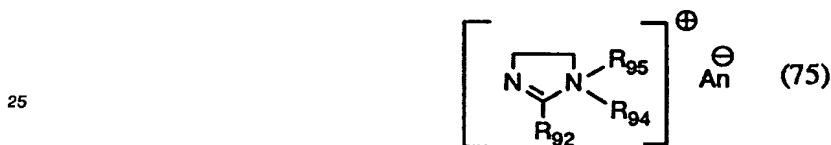
5 Preferred imidazoline cationic fabric softening agents are those having the formula:



15 in which R_{91} is hydrogen or C_1 - C_4 alkyl; R_{92} is a C_8 - C_{30} aliphatic residue; R_{93} is $-C_2H_4-O(C=O)-R_{92}$ or $-C_2H_4-NH(C=O)-R_{92}$; and An^{\ominus} has its previous significance.

Preferably R_{91} is hydrogen or methyl; R_{92} is C_{14} - C_{18} alkyl or C_{14} - C_{18} alkenyl; and R_{93} is $-C_2H_4-O-(C=O)-C_{14}-C_{18}$ alkyl or $-C_{14}-C_{18}$ alkenyl, or $-C_2H_4-NH(C=O)-C_{14}-C_{18}$ alkyl or $-C_{14}-C_{18}$ alkenyl.

20 Other preferred imidazoline cationic fabric softening agents are those having the formula:



in which R_{92} and An^{\ominus} have their previous significance; R_{94} and R_{95} , independently, are a C_8 - C_{30} aliphatic residue, C_1 - C_4 alkyl, C_1 - C_4 halogenoalkyl, C_1 - C_4 hydroxyalkyl or a group $-C_2H_4-N(R_{96})-C(=O)-R_{97}$ in which R_{96} is hydrogen or C_8 - C_{30} alkyl and R_{97} is hydrogen or C_1 - C_4 alkyl.

Preferably R_{92} is C_{14} - C_{18} alkyl or C_{14} - C_{18} alkenyl; R_{94} is C_{14} - C_{18} alkyl, C_{14} - C_{18} alkenyl, C_1 - C_4 alkyl, C_1 - C_4 halogenoalkyl or C_1 - C_4 hydroxyalkyl; and R_{95} is a group $-C_2H_4-N(R_{96})-C(=O)-R_{97}$ in which R_{96} and R_{97} have their previous significance.

35 Preferred anions An^{\ominus} include chloride, bromide, iodide, fluoride, sulfate, methosulfate, nitrite, nitrate or phosphate anions, as well as carboxylate anions such as acetate, adipate, phthalate, benzoate, stearate or oleate anions.

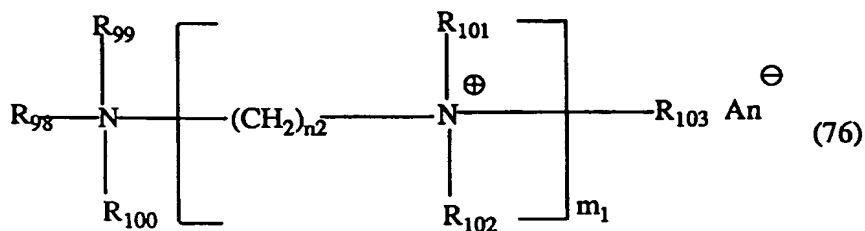
Specific examples of preferred compounds of formula (74) include:

2-tallow-1-(2-stearoyloxyethyl)-imidazoline chloride,
40 2-tallow-1-(2-stearoyloxyethyl)-imidazoline sulfate,
2-tallow-1-(2-stearoyloxyethyl)-imidazoline methosulfate,
2-tallow-1-methyl-3-(2-stearoylamidoethyl)-imidazoline chloride,
2-tallow-1-methyl-3-(2-stearoylamidoethyl)-imidazoline sulfate and
2-tallow-1-methyl-3-(2-stearoylamidoethyl)-imidazoline methosulfate.

45 Specific examples of preferred compounds of formula (75) include:

2-heptadecyl-1-methyl-1-oleylamidoethyl-imidazolinium-metho-sulfate,
2-heptadecyl-1-methyl-1-(2-stearoylamido)ethyl-imidazolinium-sulfate,
2-heptadecyl-1-methyl-1-(2-stearoylamido)ethyl-imidazolinium- chloride
2-coco-1-(2-hydroxyethyl)-1-benzyl-imidazolinium-chloride
50 2-coco-1-(2-hydroxyethyl)-1-(4-chlorobutyl)-imidazolinium-chloride
2-coco-1-(2-hydroxyethyl)-1-octadecenyl-imidazolinium-chloride
2-tallow-1-(2-hydroxyethyl)-1-benzyl-imidazolinium-chloride
2-tallow-1-(2-hydroxyethyl)-1-(4-chlorobutyl)-imidazolinium-chloride
2-heptadecenyl-1-(2-hydroxyethyl)-1-(4-chlorobutyl)-imidazolinium-chloride
55 2-heptadecenyl-1-(2-hydroxyethyl)-1-benzyl-imidazolinium-chloride and
2-heptadecenyl-1-(2-hydroxyethyl)-1-octadecyl-imidazolinium-chloride

One class of preferred quaternary ammonium compounds is that having the formula:



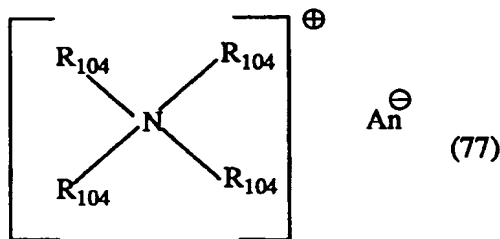
in which R_{98} is a C_8 - C_{30} aliphatic residue, R_{99} , R_{100} , R_{101} , R_{102} and R_{103} , independently, are hydrogen, C_1 - C_4 alkyl or C_1 - C_4 hydroxyalkyl, An^{\ominus} has its previous significance, m_1 is an integer from 1 to 5 and n_2 has its previous significance.

Preferred compounds of formula (76) are those in which R_{98} is C_{12} - C_{18} alkyl and R_{99} , R_{100} , R_{101} , R_{102} and R_{103} , independently, are C_1 - C_4 alkyl, especially methyl.

Specific examples of preferred compounds of formula (76) are:

N-(tallow)-N,N,N',N'-tetramethyl-1,3-propanediammoniumdimethosulfate
 N-(tallow)-N,N',N'-trimethyl-1,3-propanediammoniumdimetho sulfate
 N-(tallow)-N,N,N',N',N'-pentamethyl-1,3-propanediammoniumdimethosulfate
 N-oleyl-N,N,N',N',N'-pentamethyl-1,3-propanediammoniumdime thosulfate
 N-stearyl-N,N,N',N',N'-pentamethyl-1,3-propanediammoniumdime thosulfate and
 N-stearyloxypropyl-N,N',N'-tris(3-hydroxypropyl)-1,3-propanediammoniumdiacetate.

A further class of preferred quaternary ammonium compounds is that having the formula:

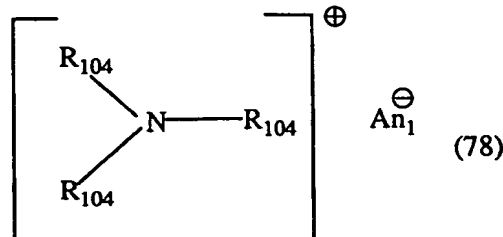


in which An^{\ominus} has its previous significance and the groups R_{104} may be the same or different and each is a C_1 - C_{30} aliphatic residue, C_1 - C_4 hydroxyalkyl, $\text{C}_2\text{H}_4\text{OC}(=\text{O})-\text{R}_{92}$, $\text{C}_2\text{H}_4\text{NHC}(=\text{O})-\text{R}_{92}$ or $\text{CH}_2\text{CH}[\text{OC}(=\text{O})-\text{R}_{92}][\text{CH}_2\text{OC}(=\text{O})-\text{R}_{92}]$, in which R_{92} has its previous significance, provided that at least one group R_{104} , and preferably two groups R_{104} are C_{14} - C_{30} alkyl, $\text{C}_2\text{H}_4\text{OC}(=\text{O})-\text{C}_{14}$ - C_{30} alkyl, $\text{C}_2\text{H}_4\text{NHC}(=\text{O})-\text{C}_{14}$ - C_{30} alkyl or $\text{CH}_2\text{CH}[\text{OC}(=\text{O})-\text{C}_{14}$ - C_{30} alkyl][$\text{CH}_2\text{OC}(=\text{O})-\text{C}_{14}$ - C_{30} alkyl]. Preferably, the remaining groups R_{104} are C_1 - C_4 alkyl, especially methyl or ethyl, or C_1 - C_4 hydroxyalkyl, especially hydroxymethyl or hydroxyethyl.

Specific examples of preferred compounds of formula (77) are:

distearyldimethylaminonium chloride
 dilauryldimethylammonium chloride
 dihexadecyldimethylammonium chloride
 distearyldimethylammonium bromide
 distearyldimethylammonium methosulfate and
 distearyldi-(isopropyl)-ammonium chloride
 distearoyl(hydroxyethyl)methylammonium methosulfate.

Preferred ester amide amine cationic fabric softening agents are those having the formula:



in which R_{104} has its previous significance and An_1^{\ominus} is an inorganic or organic acid from which an anion An^{\ominus} is derived, wherein An^{\ominus} has its previous significance, provided that at least one group R_{104} , and preferably two groups R_{104} are C_{14} - C_{30} alkyl, $(\text{CH}_2)_n\text{OC}(=\text{O})\text{-C}_{14}\text{-C}_{30}$ alkyl, $(\text{CH}_2)_{n_2}\text{NHC}(=\text{O})\text{-C}_{14}\text{-C}_{30}$ alkyl or $\text{CH}_2\text{CH}[\text{OC}(=\text{O})\text{-C}_{14}\text{-C}_{30}\text{alkyl}][\text{CH}_2\text{OC}(=\text{O})\text{-C}_{14}\text{-C}_{30}\text{alkyl}]$, in which n_2 has its previous significance. Preferably, the remaining groups R_{104} are $\text{C}_1\text{-C}_4$ alkyl, especially methyl or ethyl, or $\text{C}_1\text{-C}_4$ hydroxyalkyl, especially hydroxymethyl or hydroxyethyl.

A preferred compound of formula (78) is:

3-stearoylamidopropyl-2-stearoyloxymethyl-methylamine hydrochloride.

In addition to the fluorescent whitening agent, the fabric care composition according to the present invention may also contain a minor proportion of one or more adjuvants. Examples of adjuvants include emulsifiers, perfumes, colouring dyes, opacifiers, UV absorbers, bactericides, nonionic surfactants, anti-gelling agents such as nitrites or nitrates of alkali metals, especially sodium nitrate, and corrosion inhibitors such as sodium silicate.

The amount of each of these optional adjuvants should not exceed 2% by weight of the composition.

The present invention also provides, as a yet further aspect, a method for the treatment of a textile article, comprising applying, to a previously washed article, a fabric rinse composition comprising 0.3 to 10% by weight of a cationic, amphoteric or anionic fluorescent whitening agent, based on the total weight of the composition, and optionally a fabric care ingredient, the remainder being substantially water.

Preferably, the fabric care ingredient is a fabric softener, a stain release or stain repellent ingredient or a water-proofing agent, which is preferably present in an amount of from 5 to 25%, especially from 10 to 20% by weight, based on the total weight of the composition.

A preferred method for the treatment of a textile article, comprises applying, to the previously washed article, a rinse cycle fabric softener composition comprising 5 to 25, preferably 10 to 20% by weight of a cationic fabric softening agent and 0.3 to 10, preferably 0.3 to 3% by weight of a cationic, amphoteric or anionic fluorescent whitening agent, each based on the total weight of the composition, the remainder being substantially water.

The use according to the present invention, in addition to providing an improvement in the SPF of the treated textile material, may also increase the useful life of the textile material so treated; for example by preserving its tear strength and/or its lightfastness.

The present invention is further illustrated by the following Examples.

A) Application of a fluorescent whitening agent from a textile treatment composition.

Examples 1 to 10

An aqueous textile finishing bath is made up having the composition:

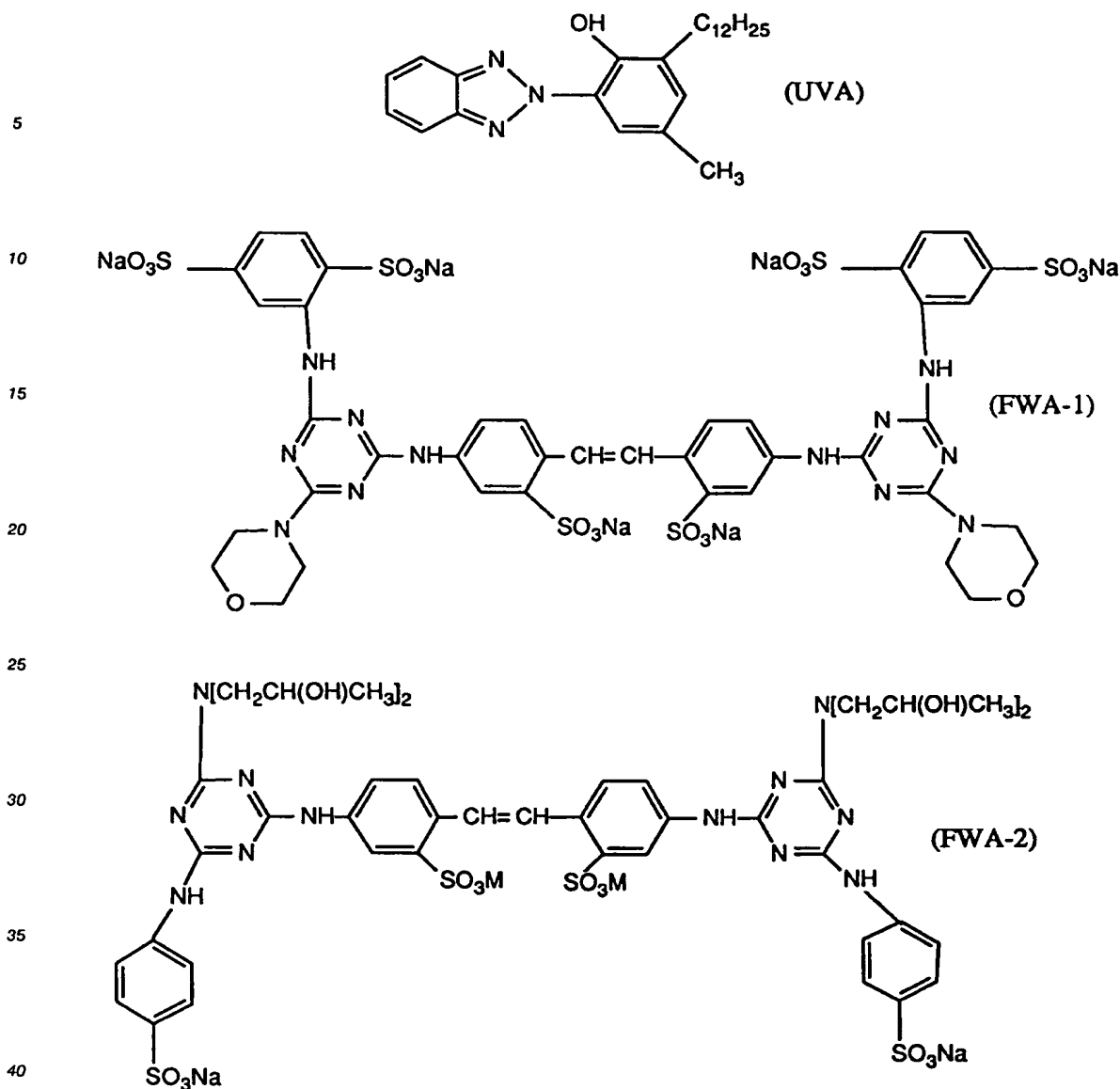
2 g/l acetic acid (40%);

40 g/l of an alkyl-modified dihydroxyethyleneurea/melamine-formaldehyde derivative;

12 g/l MgCl_2 ; and

30 g/l of an emulsion of fatty acid amides.

To separate samples of this bath are added, in the amounts shown in the following Table one or more of the following active substances (AS):



Separate samples of bleached, mercerised cotton (poplin) of density 0.68 g/cm³ and thickness 0.20 mm, are then foularded (70 % liquor uptake) with the various finishing baths, at pH 4-5. Drying of the samples of cotton is effected for 3 minutes at 110 °C. followed by thermofixing for 4 minutes at 150 °C.

The whiteness (GW) of the treated samples is measured with a DCI/SF 500 spectrophotometer according to the Ganz method. The Ganz method is described in detail in the Ciba-Geigy Review, 1973/1, and also in the article "Whiteness Measurement", ISCC Conference on Fluorescence and the Colorimetry of Fluorescent Materials, Williamsburg, February 1972, published in the Journal of Color and Appearance, 1, No.5 (1972).

The Sun Protection Factor (SPF) is determined by measurement of the UV light transmitted through the swatch, using a double grating spectrophotometer fitted with an Ulbricht bowl. Calculation of SPF is conducted as described by B.L.Difley and J.Robson in J. Soc. Cosm. Chem. 40 (1989), pp. 130-131.

The results are shown in the following Table 1.

Table 1

Example	AS	Concentration of AS		GW	SPF
		g/l in bath	% on substrate		
-	-	-	-	62	1.9
-	UVA	10	0.35	57	11.2
-	UVA	20	0.70	53	17.3
-	UVA	30	1.05	34	17.4
1	UVA FWA-1	10 10	0.35 0.13	175	15.8
2	UVA FWA-1	20 10	0.70 0.13	171	16.5
3	UVA FWA-1	10 20	0.35 0.25	177	18.0
4	UVA FWA-2	10 8	0.35 0.14	167	18.3
5	UVA FWA-2	20 8	0.70 0.14	134	21.7
6	UVA FWA-2	10 16	0.35 0.28	178	15.9
7	FWA-1	10	0.13	227	11.7
8	FWA-1	20	0.25	229	15.2
9	FWA-2	8	0.14	223	13.0
10	FWA-2	16	0.28	215	13.2

The results in the Table 1 demonstrate clearly the improvement in the SPF value of a substrate treated according to the method of the present invention.

Examples 11 to 20

Using the general procedure described in Examples 1 to 10, samples of poplin ("Supraluxe" ex Walser AG; density 0.62 g/cm³; thickness 0.17 mm) are foularded (70 % liquor uptake) with the various finishing baths, at pH 4-5. Drying of the samples of poplin is effected for 3 minutes at 110 °C. followed by thermofixing for 4 minutes at 150 °C.

The whiteness (GW) and SPF of the respective treated samples are measured as before.

In order to evaluate the wash permanency of the textile treatment applied, the respective treated poplin samples are washed ten times and the whiteness (GW) and SPF values are determined after the first, fifth and tenth washes.

50g of the poplin swatches are washed in 1 litre of tap water (12 ° German hardness) containing 4g of a detergent having the following composition (weight %):

8.0% Sodium alkylbenzene sulfonate

2.9% Tallow alcohol-tetradecane-ethylene glycol ether (14 mols EO)

3.5% Sodium soap

43.8% Sodium tripolyphosphate

7.5% Sodium silicate

1.9% Magnesium silicate

1.2% Carboxymethyl cellulose

0.2% EDTA

21.2% Sodium sulfate

x% fluorescent whitening agent (FWA) by weight on detergent

Water to 100%.

The washing is conducted at 60° C. over 15 minutes. The swatches are then rinsed under cold running tap water for 30 seconds and dried.

The results are set out in the following Table 2.

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Ex.	AS	Concentration of AS		GW after washing				SPF after washing			
		g/l in bath	% on sub.	0x	1x	5x	10x	0x	1x	5x	10x
-	-	-	-	63	71	75	76	4	5	5	5
-	UVA	10	0.35	59	70	69	72	25	18	13	11
-	UVA	20	0.70	55	67	68	71	47	31	30	19
-	UVA	30	1.05	58	68	72	72	81	45	47	30
-	UVA	40	1.40	52	65	70	70	99	46	50	37
11	UVA FWA-1	10 10	0.35 0.13	176	152	133	133	57	19	13	10
12	UVA FWA-1	20 10	0.70 0.13	147	123	109	108	67	39	24	16
13	UVA FWA-1	10 20	0.35 0.25	203	193	160	155	51	19	13	13
14	UVA FWA-2	10 8	0.35 0.14	178	178	171	166	41	26	17	19
15	UVA FWA-2	20 8	0.70 0.14	149	141	138	136	82	62	34	29
16	UVA FWA-2	10 16	0.35 0.28	198	210	208	208	59	26	16	18
17	FWA-1	10	0.13	222	205	197	178	24	9	8	7
18	FWA-1	20	0.25	236	227	203	209	31	13	6	7
19	FWA-2	8	0.14	216	215	216	206	31	19	16	10
20	FWA-2	16	0.28	226	239	233	235	42	19	13	16

The results in Table 2 demonstrate clearly the improvement in the SPF value of a substrate treated according to the method of the present invention and, moreover, that the use of a combination of UVA and FWA leads to unexpected synergistic SPF values.

Example 21

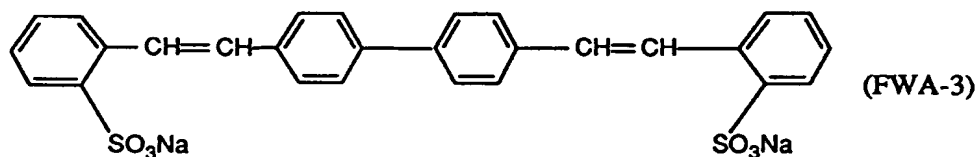
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A 5 g. sample of poplin ("Supraluxe" ex Walser AG; density 0.62 g/cm³) is foularded (80% liquor uptake) with an aqueous bath containing:

4 g/l sodium bicarbonate and

12.5 g/l of a fluorescent whitening agent having the formula:

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to provide a concentration of 1% by weight of active substance on the poplin substrate.

Foularding is conducted at alkaline pH.

Drying of the treated sample is carried out at 80 °C. for 2 minutes.

The treated poplin has an SPF rating of above 40, whereas that of the untreated poplin is 4.

Example 22

A 5 g. sample of poplin ("Supraluxe" ex Walser AG; density 0.62 g/cm³) is foularded (80% liquor uptake) with an aqueous bath containing:

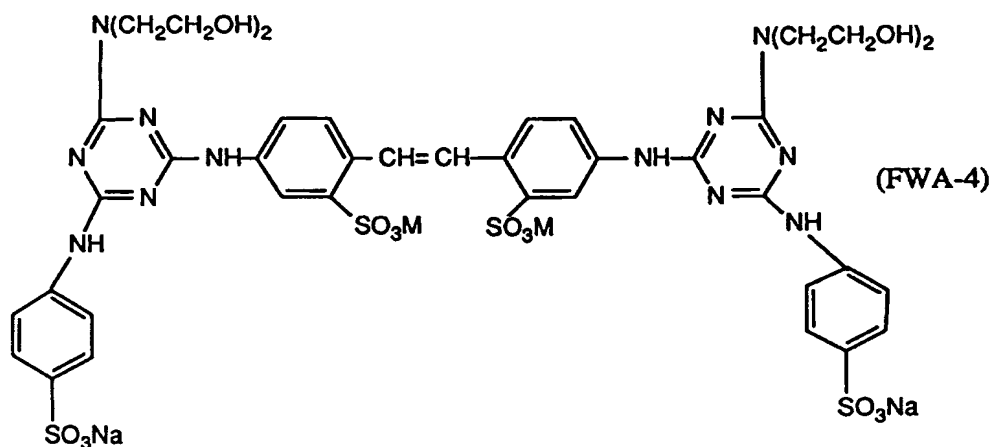
2 g/l acetic acid (40%)

40 g/l of an alkyl-modified dihydroxyethyleneurea/melamine-formaldehyde derivative;

12 g/l MgCl₂;

30 g/l of an emulsion of fatty acid amides and

12.5 g/l of a fluorescent whitening agent having the formula:



to provide a concentration of 1% by weight of active substance on the poplin substrate.

Foularding is conducted at a pH of 6-7.

Drying of the treated sample is carried out at 80 °C. for 2 minutes, followed by thermofixing for 4 minutes at 150 °C.

The treated poplin has an SPF rating of above 30, whereas that of the untreated poplin is 4.

Example 23

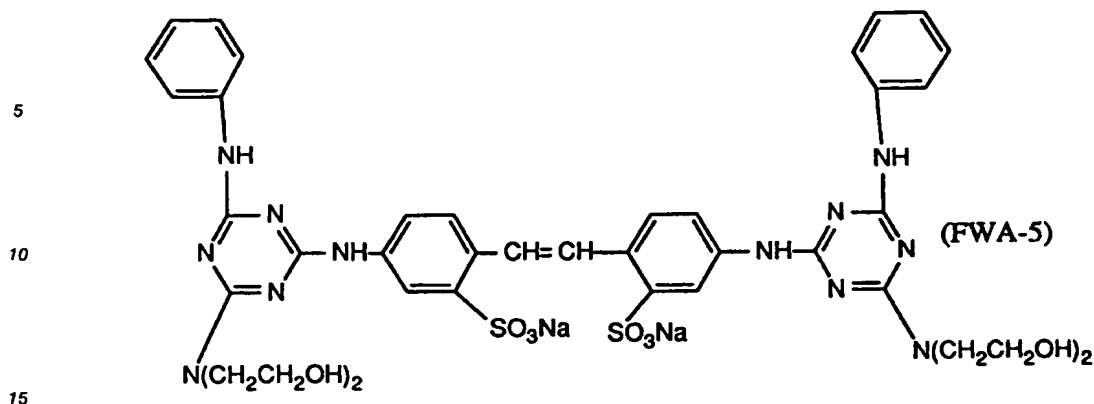
A 5 g. sample of poplin ("Supraluxe" ex Walser AG; density 0.62 g/cm³) is treated with an aqueous bath containing:

3 g/l anhydrous sodium sulfate

3 g/l caustic soda flake

1.5 g/l nonylphenol ethoxylate (7 mols EO) and

1% by weight of poplin fabric of a fluorescent whitening agent having the formula:



the treatment is conducted at 95 ° C. over 30 minutes and at a liquor ratio of 40:1, using a laboratory dyeing machine.

The treated poplin is rinsed successively with hot or cold water and dried.

The treated poplin has an SPF rating of above 30, whereas that of the untreated poplin is 4.

B) Application of a fluorescent whitening agent from a detergent composition.

Examples 24 to 29

50g of bleached, mercerised cotton swatches are washed in 1 litre of tap water (12 ° German hardness) containing 4g of a detergent having the following composition (weight %):

8.0% Sodium alkylbenzene sulfonate

2.9% Tallow alcohol-tetradecane-ethylene glycol ether (14 mols EO)

3.5% Sodium soap

43.8% Sodium tripolyphosphate

7.5% Sodium silicate

1.9% Magnesium silicate

1.2% Carboxymethyl cellulose

0.2% EDTA

21.2% Sodium sulfate

x% fluorescent whitening agent (FWA) by weight on detergent

Water to 100%.

The washing is conducted at 40 ° C. over 15 minutes. The swatches are then rinsed under cold running tap water for 30 seconds and dried. The wash treatment is repeated three times. After the third wash, the swatches are ironed at 160 ° C.

The results obtained are set out in the following Table 3.

Table 3

Example	FWA	Concentration FWA	W	SPF
-	-	-	79	1.6
24	Compound (31)	0.2%	211	6.1
25	Compound (32)	0.2%	202	3.9
26	Compound (36)	0.2%	200	5.2
27	Compound (37)	0.1%	207	4.2
28	Compound (40)	0.1%	201	3.4
29	Compound (45)	0.1%	208	3.1

SPF values are the average of 3 measurements at various points on the swatches. The relative variation of the results lies within a range of from about plus or minus 10%.

Compared with the control experiment (no FWA), the SPF values obtained to the invention are 2-4 times higher, after only 3 washes.

Example 30

A bleached, mercerised cotton swatch is dyed by the exhaustion method using 0.95% by weight on the fabric of a commercial blue reactive dye. The dyeing is conducted at a liquor ratio of 20:1, the temperature is raised from 25° to 100°C. over 40 minutes, and then held for 1 hour at 100°C. with the addition of 15g/l of sodium sulphate, before applying a final cold rinse.

The SPF of the dyed goods is then determined by the method described in Examples 24 to 29.

The dyed goods are then washed in the manner described in Examples 24 to 29 using the same detergent composition. The FWA compound used in the detergent is the compound of formula (40), at a level of 0.1 weight % of active substance, based on the weight of the detergent. The SPF value of the washed goods and also of goods washed with the same detergent containing no FWA (for control purposes) is determined after 1, 3, 5 and 10 washes. The results are set out in the following Table 4.

Table 4

Example	number of washes	SPF	
		without fwa	with fwa
-	control pre-wash	23.7	23.7
30	one	22.5	23.8
	three	22.0	25.9
	five	20.9	26.9
	ten	19.8	28.7

The results in Table 4 demonstrate that the SPF of dyed fabrics can decrease significantly when the fabrics are washed with a detergent which does not contain an FWA. By contrast, washing with a detergent containing a compound of formula (40) not only eliminates this loss of protection against aggressive sunlight radiation, but also actually increases the SPF protection with successive washings.

C) Application of a fluorescent whitening agent from a rinse composition.

Example 31

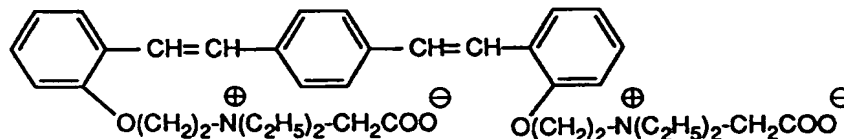
The following rinse cycle softener base composition is made up:

7.0g. distearyldimethylammonium chloride (72% active ingredient)

0.5g. fatty alcohol ethoxylate

92.5g. deionised water.

To this is added 0.3g., 0.9g. or 2.7g., respectively, of the amphoteric fluorescent whitening agent of formula:



Example 32

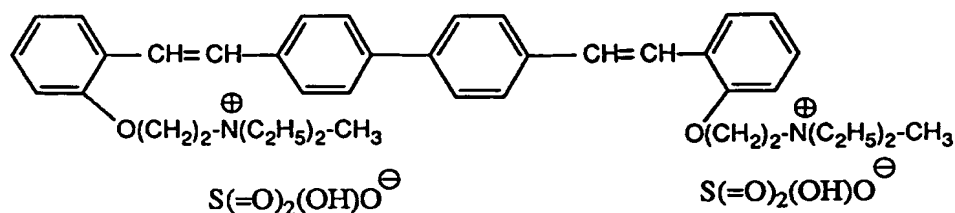
The following rinse cycle softener base composition is made up:

7.0g. distearyldimethylammonium chloride

0.5g. fatty alcohol ethoxylate

92.5g. deionised water.

To this is added 0.3g., 0.9g. or 2.7g., respectively, of the cationic fluorescent whitening agent of formula:

**Examples 33 and 34**

5g. of cotton fabric are first washed with 4g/l of ECE standard detergent using a liquor ratio of 1:20 at 60 °C. The washed goods are then rinsed and are subjected, while still wet, to a rinse softener treatment. The amount of the rinse cycle softener base composition of Example 1 or 2 used is 5g/l. The liquor ratio is 1:40 using tap water and the treatment is effected at 25 °C. for 10 minutes. The softener-treated goods are then spin-dried at 60 °C.

The whiteness and SPF values of the dried softener-treated goods are measured.

The dried softener-treated goods are then re-washed using the same detergent and washing conditions that are used for the initial wash except that, after the rinse, the re-washed goods are spin-dried at 60 °C. without being subjected to a rinse softener treatment. The whiteness and SPF values of the re-washed, dried goods are measured.

The results are shown in the following Table 5.

Table 5

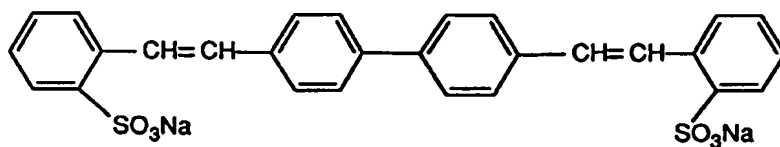
Example	Rinse Composition	Conc. FWA	Without re-wash		With re-wash	
			GW	SPF	GW	SPF
-	control (no FWA)	-	67	3	75	3
33	Rinse of Example 31	0.3	194	9	181	8
		0.9	197	15	199	11
		2.7	169	24	200	16
34	Rinse of Example 32	0.3	199	14	182	13
		0.9	206	17	202	20
		2.7	193	29	193	26

The concentration of FWA denotes the concentration of active FWA compound based on the total weight of the rinse formulation.

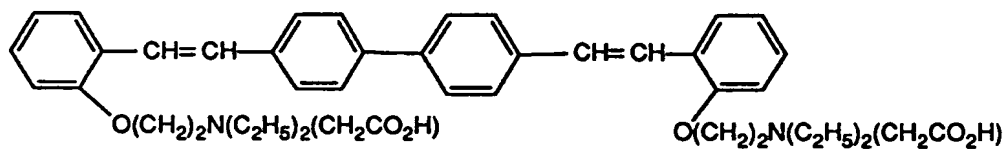
The results in Table 5 clearly demonstrate the improvement in the Gas Whiteness and SPF values of a cotton substrate treated with a rinse composition according to the present invention, both before and after a subsequent re-wash.

Similar results are obtained when the fluorescent whitening agent used in Example 31 or 32 is replaced by a compound having one of the following formulae:

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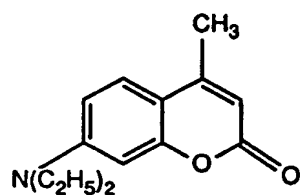


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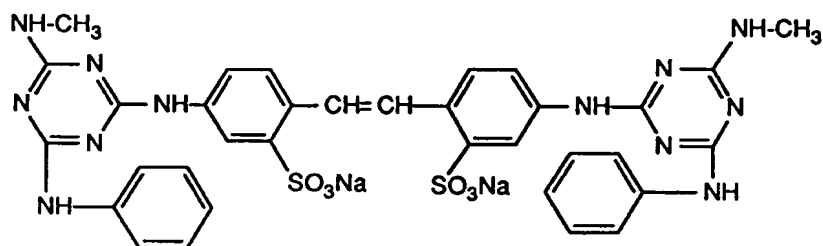
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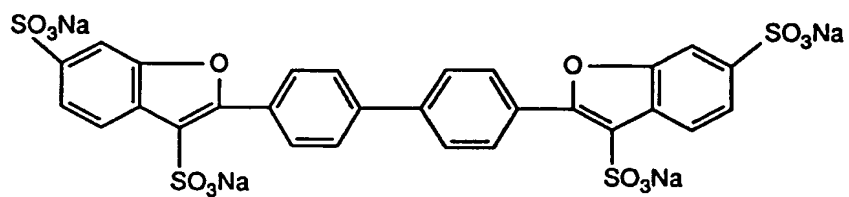
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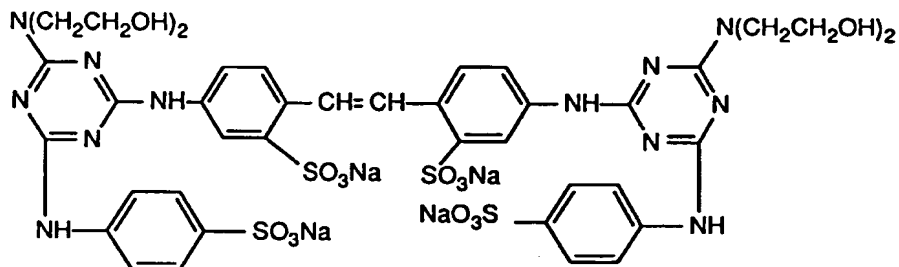
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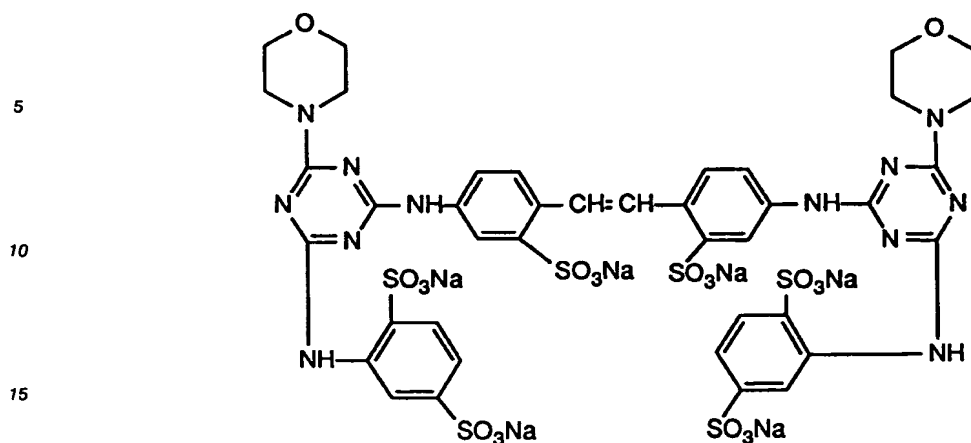


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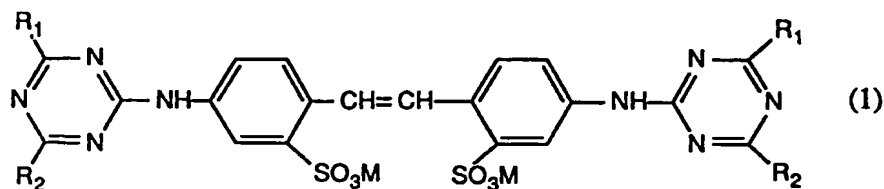


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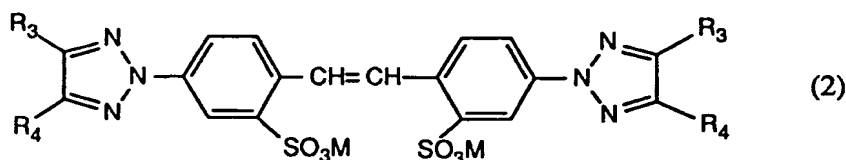
20 Claims

1. A method of improving the sun protection factor (SPF) of textile fibre material, comprising treating the textile fibre material with a composition comprising at least one fluorescent whitening agent which absorbs radiation in the wavelength range 280-400 nm.
2. A method according to claim 1 in which the textile fibre material treated is composed of wool, polyamide, cotton, polyester, polyacrylic, silk, polypropylene or a mixture thereof.
3. A method according to claim 2 in which the textile fibre material is in the form of endless filaments (stretched or unstretched), staple fibres, flocks, hanks, textile filament yarns, threads, nonwovens, felts, waddings, flocked structures or woven textile or bonded textile fabrics or knitted fabrics.
4. A method according to any of the preceding claims in which the textile fibre material is contacted with a composition which is:
 - a) an aqueous textile finishing composition;
 - b) a detergent composition; or
 - c) a post-wash fabric care composition.
5. A method according to any of the preceding claims in which the amount of fluorescent whitening agent present in the composition ranges from 0.005 to 20 %, based on the weight of the textile fibre material.
6. A method according to claim 5 in which the composition is an aqueous textile finishing composition and the amount of fluorescent whitening agent present in the composition ranges from 0.01 to 3%; or the composition is a detergent composition and the amount of fluorescent whitening agent present in the composition ranges from 0.005 to 2%; or the composition is a post-wash fabric care composition and the amount of fluorescent whitening agent present in the composition ranges from 0.1 to 20%; each based on the weight of the textile fibre material.
7. A method according to any of claims 4 to 6 in which the composition is an aqueous textile finishing composition and the fluorescent whitening agent used is a 4,4'-bis-(triazinylamino)-stilbene-2,2'-disulfonic acid, 4,4'-bis-(triazol-2-yl)stilbene-2,2'-disulfonic acid, 4,4'-(diphenyl)-stilbenes, 4,4'-distyryl-biphenyl, 4-phenyl-4'-benzoxazolyl-stilbene, stilbenyl-naphthotriazoles, 4-styryl-stilbene, bis-(benzoxazol-2-yl) derivatives, bis-(benzimidazol-2-yl) derivative, coumarine, pyrazoline, naphthalimide, triazinyl-pyrene, 2-styryl-benzoxazole- or -naphthoxazole derivative, benzimidazole-benzofuran or oxanilide derivative.
8. A method according to claim 7 in which the 4,4'-bis-(triazinylamino)-stilbene-2,2'-disulfonic acid is one having the formula:



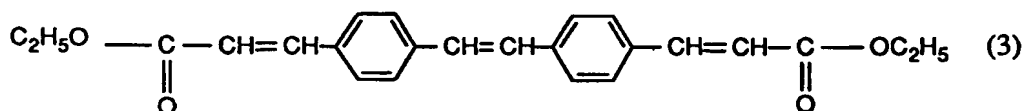
10 in which R₁ and R₂, independently, are phenyl, mono- or disulfonated phenyl, phenylamino, mono- or disulfonated phenylamino, morpholino, -N(CH₂CH₂OH)₂, -N(CH₃)(CH₂CH₂OH), -NH₂, -N(C₁-C₄-alkyl)₂, -OCH₃, -Cl, -NH-CH₂CH₂SO₃H or -NH-CH₂CH₂OH; and M is H, Na, K, Ca, Mg, ammonium, mono-, di-, tri- or tetra-C₁-C₄-alkylammonium, mono-, di- or tri-C₁-C₄-hydroxyalkylammonium or ammonium that is di- or tri-substituted with by a mixture of C₁-C₄-alkyl and C₁-C₄-hydroxyalkyl groups.

- 15 9. A method according to claim 7 in which the 4,4'-bis-(triazol-2-yl)stilbene-2,2'-disulfonic acid is one having the formula:

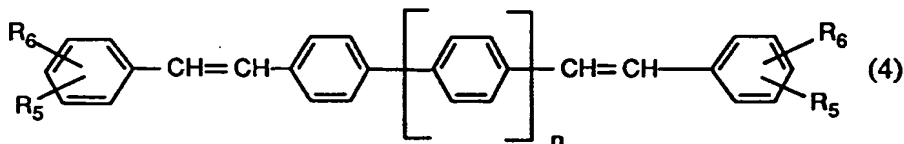


in which R₃ and R₄, independently, are H, C₁-C₄-alkyl, phenyl or monosulfonated phenyl; and M is as defined in claim 8.

- 30 10. A method according to claim 7 in which the 4,4'-(diphenyl)-stilbene is one having the formula:

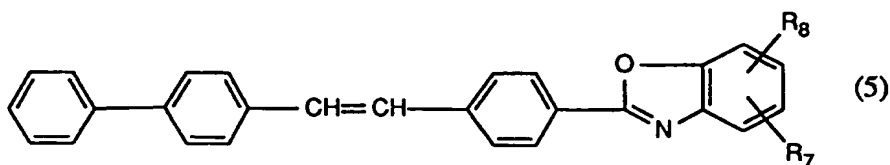


- 40 11. A method according to claim 7 in which the 4,4'-distyryl-biphenyl used has the formula:



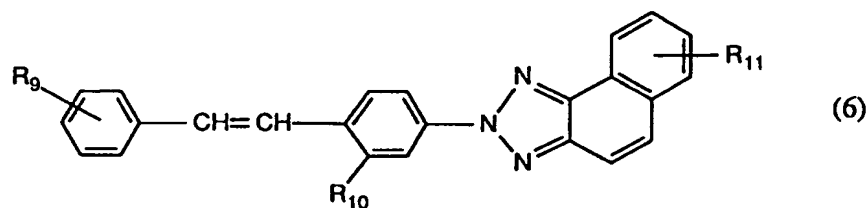
in which R₅ and R₆, independently, are H, SO₃M, SO₂N(C₁-C₄-alkyl)₂, O-(C₁-C₄-alkyl), CN, Cl, COO-(C₁-C₄-alkyl), CON(C₁-C₄-alkyl)₂ or O(CH₂)₃N[⊖](CH₃)₂An[⊖], in which An[⊖] is an anion of an organic or inorganic acid; and n is 0 or 1.

- 50 12. A method according to claim 7 in which the 4-phenyl-4'-benzoxazolyl-stilbene has the formula:



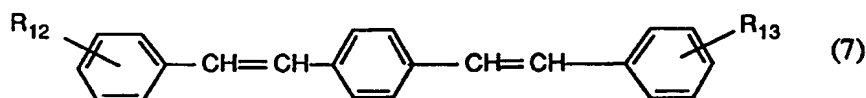
10 in which R_7 and R_8 , independently, are H, Cl, C_1 - C_4 -alkyl or SO_2 - C_1 - C_4 -alkyl.

13. A method according to claim 7 in which a stilbenyl-naphthotriazole used is one of formula:



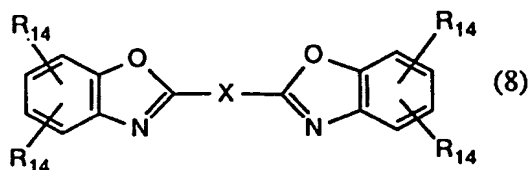
in which R_9 is H or Cl; R_{10} is SO_3M , $SO_2N(C_1-C_4-alkyl)_2$, SO_2O -phenyl or CN; R_{11} is H or SO_3M ; and M is as defined in claim 8.

25 14. A method according to claim 7 in which a 4-styryl-stilbene used is one of formula:



35 in which R_{12} and R_{13} , independently, are H, SO_3M , $SO_2N(C_1-C_4-alkyl)_2$, O -(C_1 - C_4 -alkyl), CN, Cl, COO -(C_1 - C_4 -alkyl), $CON(C_1-C_4-alkyl)_2$ or $O(CH_2)_3N^{\oplus}(CH_3)_2An^{\ominus}$ in which An^{\ominus} is as defined in claim 11.

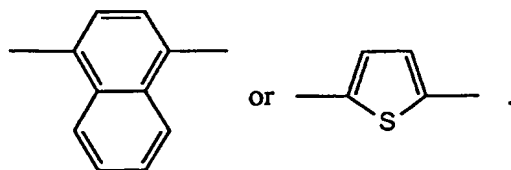
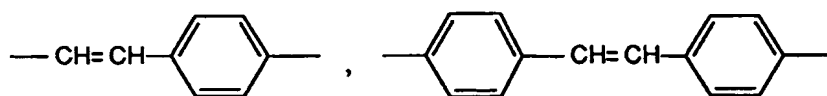
15. A method according to claim 7 in which a bis-(benzoxazol-2-yl) derivative used having the formula:



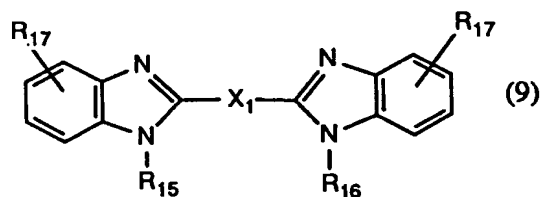
in which R_{14} , independently, is H, $C(CH_3)_3$, $C(CH_3)_2$ -phenyl, C_1 - C_4 -alkyl or COO - C_1 - C_4 -alkyl, and X is $-CH=CH-$ or a group of formula:

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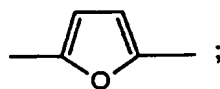
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16. A method according to claim 7 in which a bis-(benzimidazol-2-yl) derivatives is used of formula:

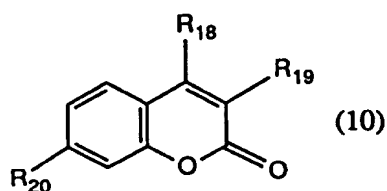


in which R_{15} and R_{16} , independently, are H, $\text{C}_1\text{--C}_4$ -alkyl or $\text{CH}_2\text{CH}_2\text{OH}$, R_{17} is H or SO_3M ; X_1 is ---CH=CH--- or a group of formula:

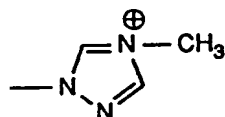


and M is as defined in claim 8.

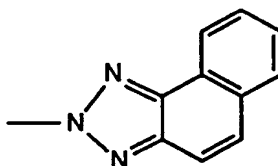
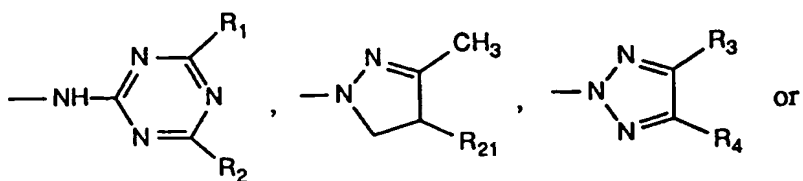
17. A method according to claim 7 in which a coumarine is used of formula:



in which R_{18} is H, Cl or CH_2COOH , R_{19} is H, phenyl, $\text{COO--C}_1\text{--C}_4$ -alkyl or a group of formula:

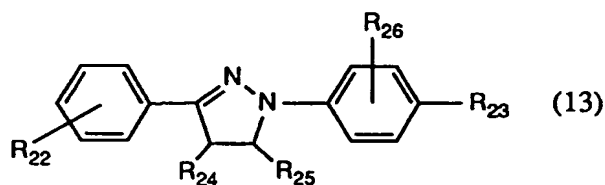


and R_{20} is $\text{O--C}_1\text{--C}_4$ -alkyl, $\text{N(C}_1\text{--C}_4\text{--alkyl)}_2$, $\text{NH--CO--C}_1\text{--C}_4$ -alkyl or a group of formula:



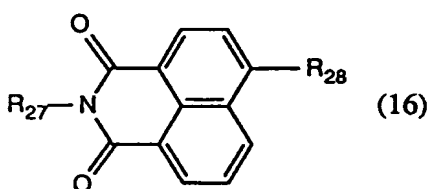
in which R_1 and R_2 are as defined in claim 7, R_3 and R_4 are as defined in claim 9 and R_{21} is H, C₁-C₄-alkyl or phenyl.

20 18. A method according to claim 7 in which a pyrazoline used is one having the formula:



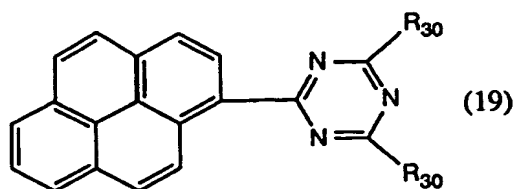
30 in which R_{22} is H, Cl or N(C₁-C₄-alkyl)₂, R_{23} is H, Cl, SO₃M, SO₂NH₂, SO₂NH-(C₁-C₄-alkyl), COO-C₁-C₄-alkyl, SO₂-C₁-C₄-alkyl, SO₂NHCH₂CH₂CH₂N⁺(CH₃)₃ or SO₂CH₂CH₂N⁺H(C₁-C₄-alkyl)₂ An⁺, R_{24} and R_{25} are the same or different and each is H, C₁-C₄-alkyl or phenyl and R_{26} is H or Cl; M is as defined in claim 8 and An⁺ is as defined in claim 11.

35 19. A method according to claim 7 in which a naphthalimide is used of formula:



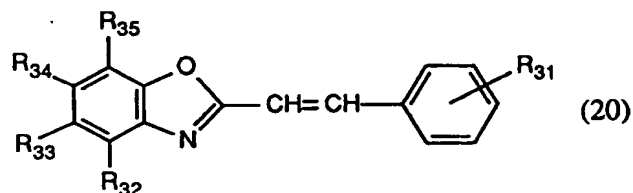
in which R_{27} is C₁-C₄-alkyl or CH₂CH₂CH₂N⁺(CH₃)₃; R_{28} is O-C₁-C₄-alkyl, SO₃M or NH-CO-C₁-C₄-alkyl; and M is as defined in claim 8.

20. A method according to claim 7 in which a triazinyl-pyrene is used of formula:



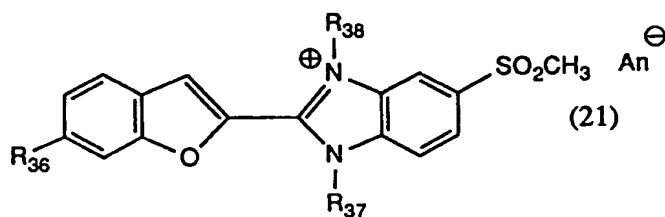
in which each R_{29} , independently, is C_1 - C_4 -alkoxy.

21. A method according to claim 7 in which a 2-styryl-benzoxazole- or -naphthoxazole derivative is used having the formula:



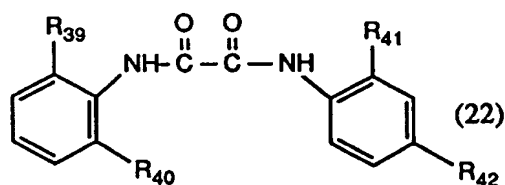
in which R_{31} is CN, Cl, COO - C_1 - C_4 -alkyl or phenyl; R_{32} and R_{33} are the atoms required to form a fused benzene ring or R_{33} and R_{35} , independently, are H or C_1 - C_4 -alkyl; and R_{34} is H, C_1 - C_4 -alkyl or phenyl.

22. A method according to claim 7 in which a benzimidazole-benzofuran derivative is used having the formula:



in which R_{36} is C_1 - C_4 -alkoxy; R_{37} and R_{38} , independently, are C_1 - C_4 -alkyl; and An^- is as defined in claim 11.

23. A method according to claim 7 in which an oxanilide derivative is used having the formula:

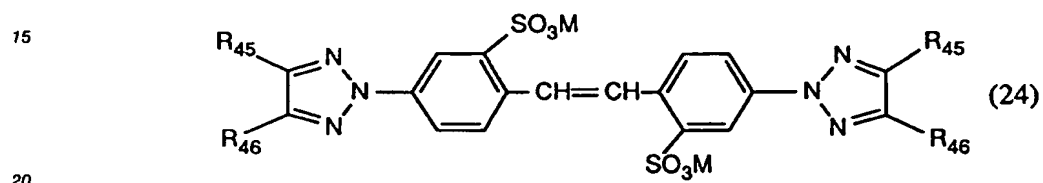
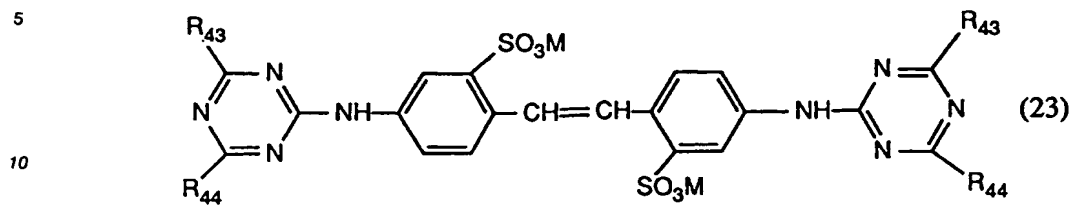


in which R_{39} is C_1 - C_4 alkoxy, R_{41} is C_1 - C_4 alkyl, C_1 - C_4 alkyl- SO_3M or C_1 - C_4 alkoxy- SO_3M in which M is as defined in claim 8, and R_{40} and R_{42} are the same and each is hydrogen, tert. butyl or SO_3M in which M is as defined in claim 8.

24. A method according to any of claims 4 to 23 in which the composition is a textile finishing composition and the fluorescent whitening agent is used:

- a) in mixtures with dyes (shading) or pigments;
- b) in mixtures with carriers, wetting agents, antioxidants, UV absorbers and/or chemical bleaching agents; or
- c) in admixture with crosslinking or finishing agents or in combination with a textile finishing process or flameproof finish, soft handle finish, antisoiling finish, antistatic finish or antimicrobial finish.

25. A method according to any of claims 4 to 6 in which the composition is a detergent composition and the fluorescent whitening agent used has one of the formulae:



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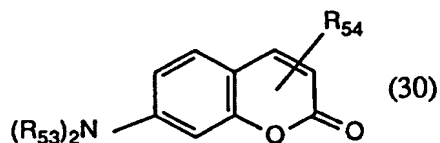
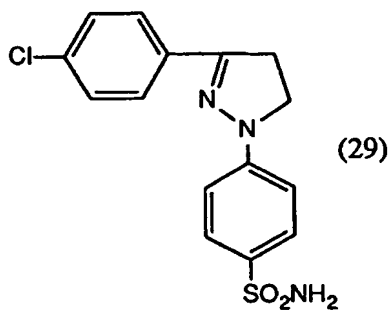
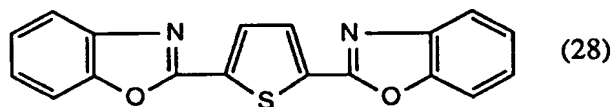
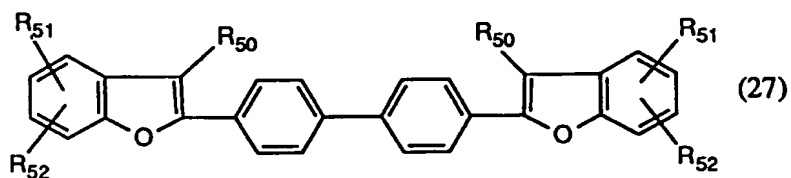
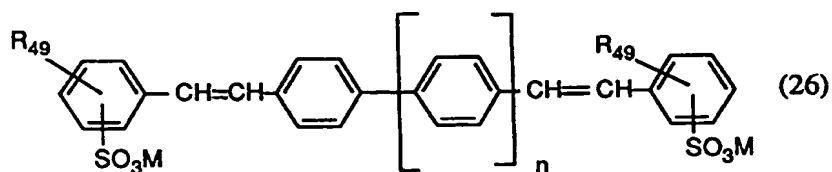
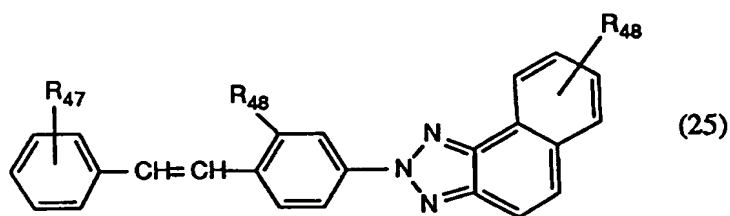
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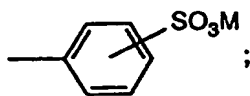
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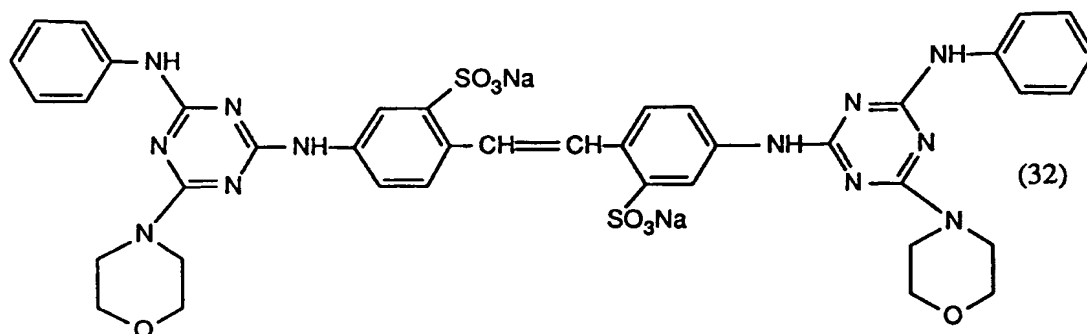
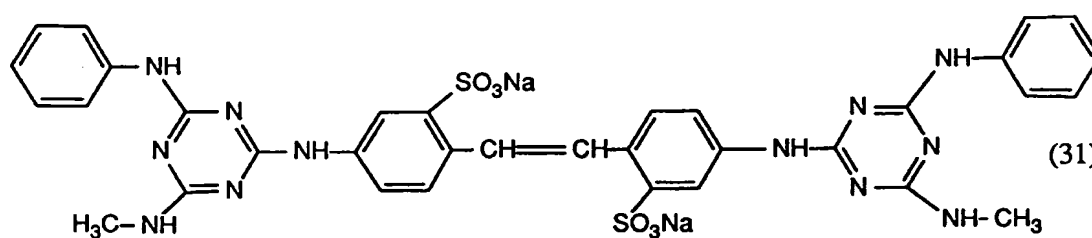


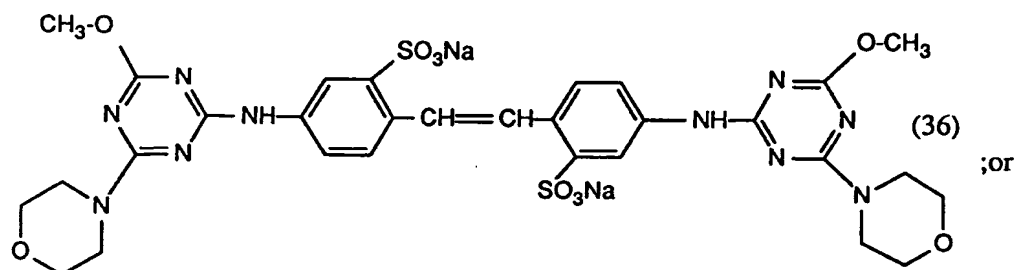
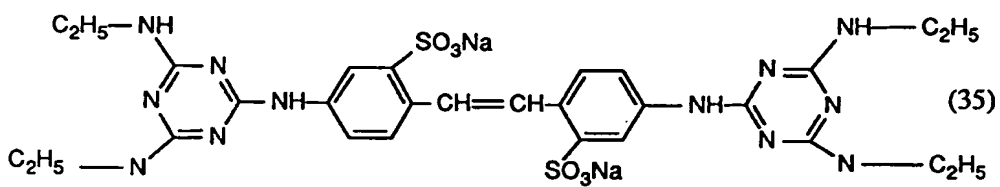
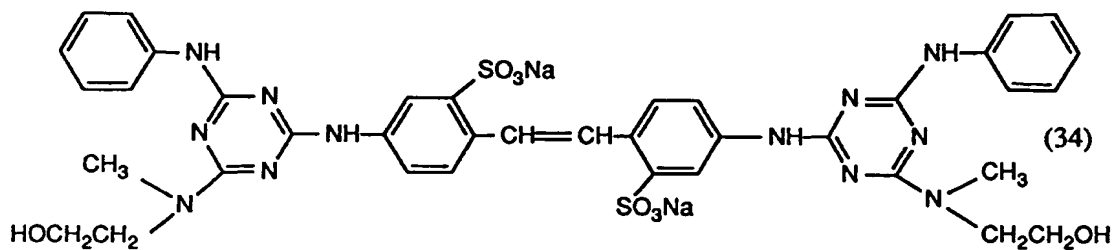
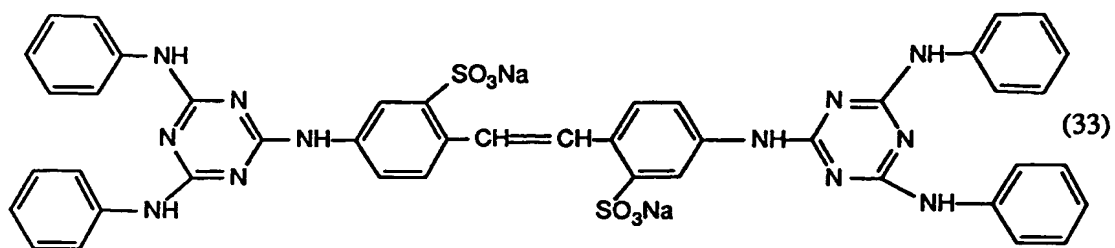
in which R_{43} and R_{44} , independently, are OH, NH_2 , O- C_1 - C_4 -alkyl, O-aryl, NH- C_1 - C_4 -alkyl, N(C_1 - C_4 -alkyl) $_2$, N(C_1 - C_4 -alkyl)(C_1 - C_4 -hydroxyalkyl), N(C_1 - C_4 -hydroxyalkyl) $_2$, NH-aryl, morpholino, S- C_1 - C_4 -alkyl-aryl, Cl or OH; R_{45} and R_{46} , independently, are H, C_1 - C_4 -alkyl, phenyl or a group of formula:



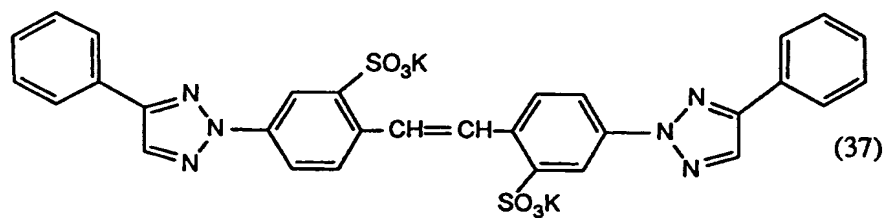
R_{47} is H, Cl or SO_3M ; R_{48} is CN, SO_3M , $S(C_1-C_4-alkyl)_2$ or $S(aryl)_2$; R_{49} is H, SO_3M , O- $C_1-C_4-alkyl$, CN, Cl, $COO-C_1-C_4-alkyl$, or $CON(C_1-C_4-alkyl)_2$; R_{50} is H, $C_1-C_4-alkyl$, Cl or SO_3M ; R_{51} and R_{52} , independently, are H, $C_1-C_4-alkyl$, SO_3M , Cl or O- $C_1-C_4-alkyl$; R_{53} is H or $C_1-C_4-alkyl$; R_{54} is H, $C_1-C_4-alkyl$, CN, Cl, $COO-C_1-C_4-alkyl$, $CON(C_1-C_4-alkyl)_2$, aryl or O-aryl; M is as defined in claim 8 and n is as defined in claim 11.

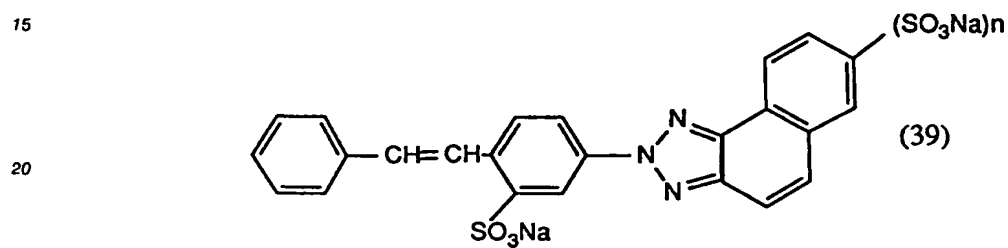
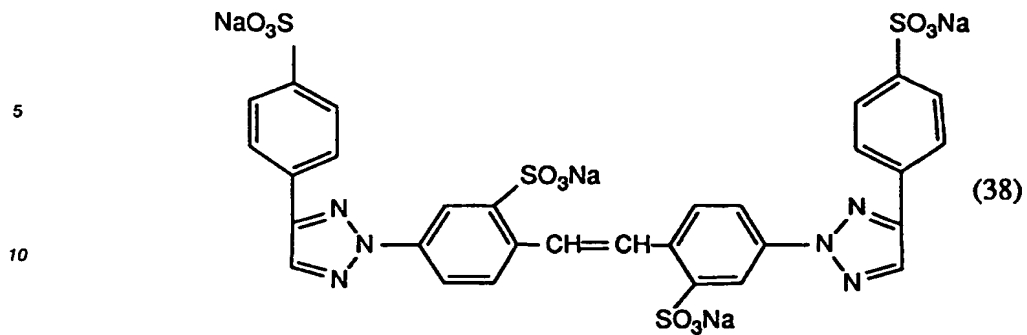
26. A method according to claim 25 in which the compound of formula (23) has the formula:



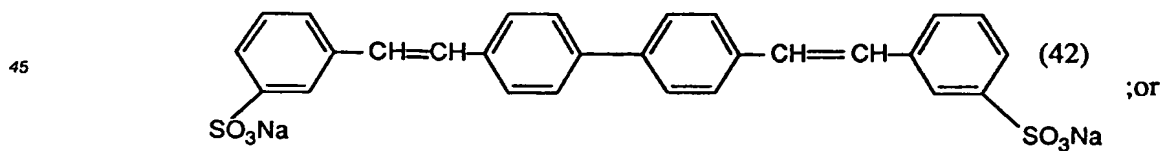
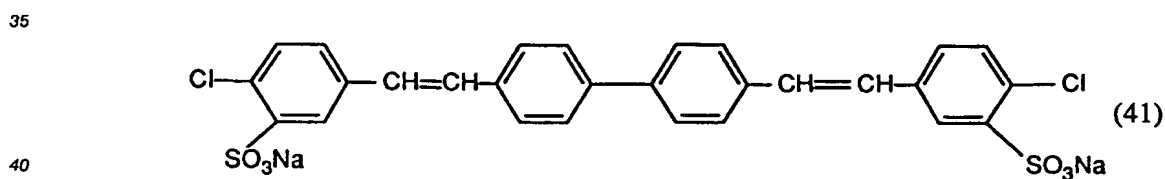
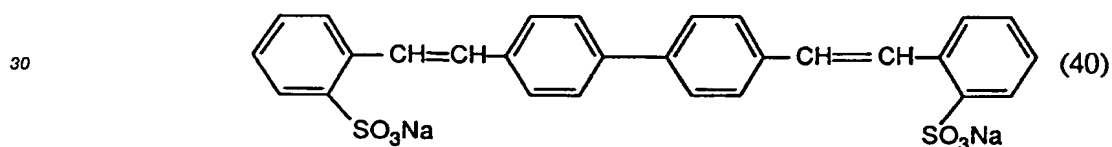


in which the compound of formula (24) has the formula:



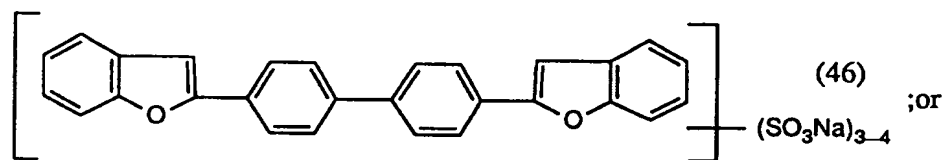
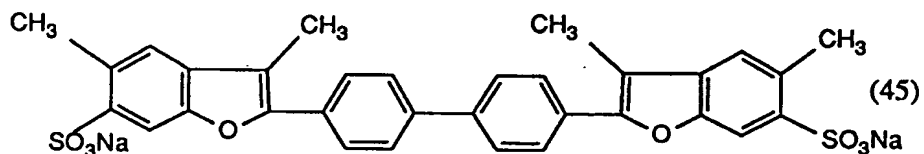
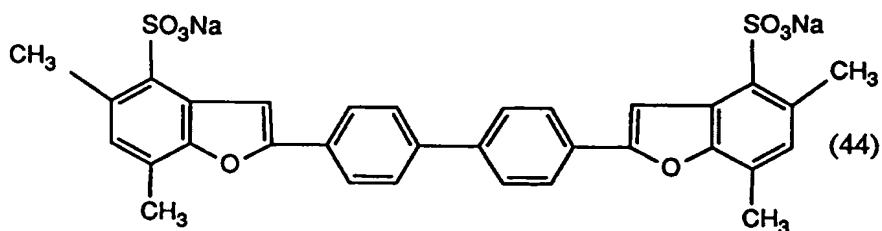
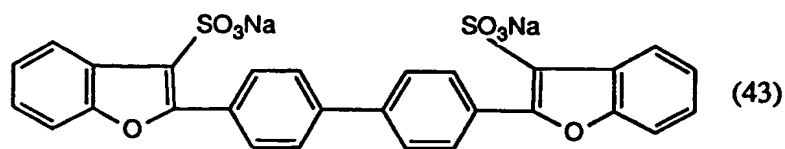


25 in which n is as defined in claim 11; or
in which the compound of formula (26) has the formula:

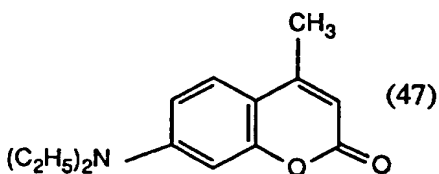


50 in which the compound of formula (27) has the formula:

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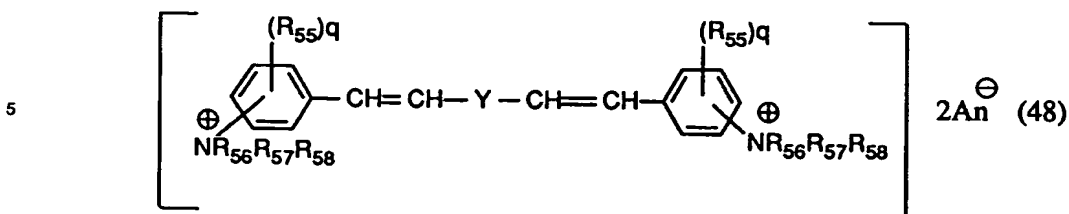
in which the compound of formula (30) has the formula:



27. A method according to any of claims 4 to 6 in which the composition is a post-wash fabric care composition and the fluorescent whitening agent is a cationic, amphoteric or anionic fluorescent whitening agent.

28. A method according to claim 27 in which the cationic fluorescent whitening agent is of the bistyrylphenyl class or phosphinic acid salt class; the amphoteric fluorescent whitening agent is of the styrene or amine oxide class; and the anionic fluorescent whitening agent is of the aminostilbene, dibenzofuranylbiophenyl or bistyrylphenyl class.

29. A method according to claim 28 in which the cationic bistyrylphenyl fluorescent whitening agent has the formula:

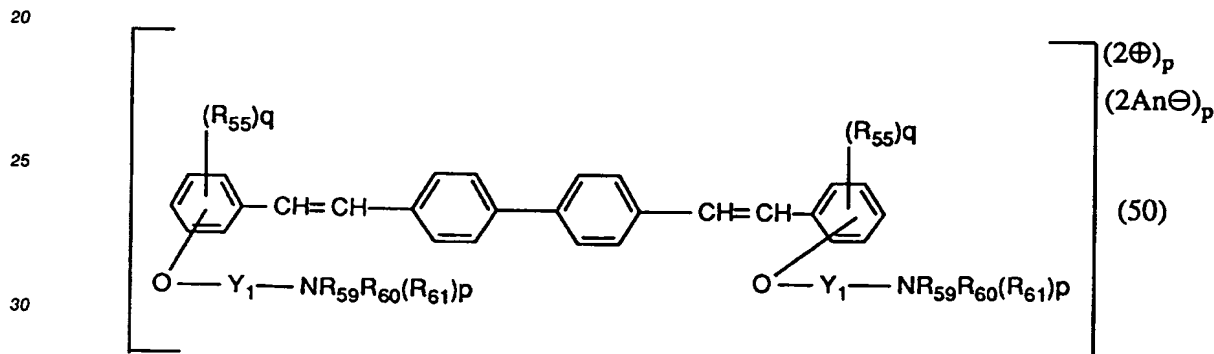


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in which Y is arylene, optionally substituted by chloro, methyl or methoxy; q is 1 or 2; R₅₅ is hydrogen, chloro, C₁-C₄-alkyl, C₁-C₄-alkoxy, cyano or C₁-C₄-alkoxycarbonyl; R₅₆ and R₅₇ are C₁-C₄-alkyl, chloroethyl, methoxyethyl, β-ethoxyethyl, β-acetoxyethyl or β-cyanoethyl, benzyl or phenylethyl; R₅₈ is C₁-C₄-alkyl, C₂-C₃-hydroxyalkyl, β-hydroxy-γ-chloropropyl, β-cyanoethyl or C₁-C₄-alkoxy-carbonylethyl; and An[⊖] is as defined in claim 11.

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30. A method according to claim 28 in which the cationic bistyrylphenyl fluorescent whitening agent has the formula:



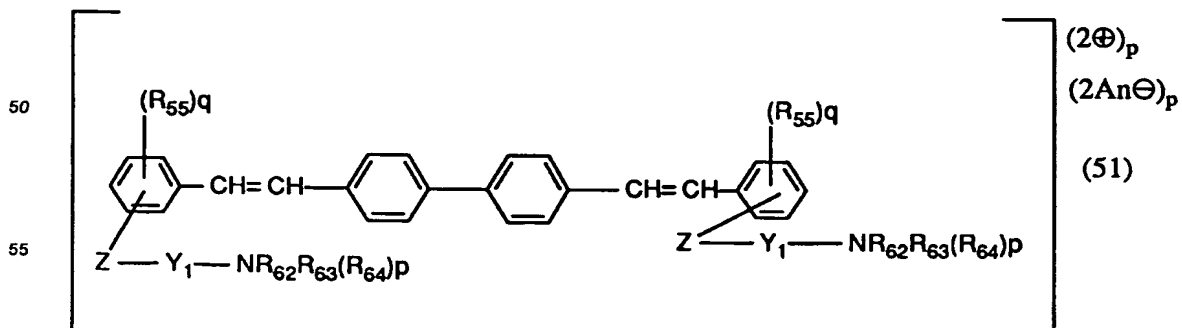
in which R₅₅ and q are as defined in claim 29; Y₁ is C₂-C₄-alkylene or hydroxypropylene; R₅₉ is C₁-C₄-alkyl or, together with R₆₀ and the nitrogen to which they are each attached, R₅₉ forms a pyrrolidine, piperidine, hexamethyleneimine or morpholine ring; R₆₀ is C₁-C₄-alkyl or, together with R₅₉ and the nitrogen to which they are each attached, R₆₀ forms a pyrrolidine, piperidine, hexamethyleneimine or morpholine ring; R₆₁ is hydrogen, C₁-C₄-alkyl, C₃-C₄-alkenyl, C₁-C₄-alkoxycarbonylmethyl, benzyl, C₂-C₄-hydroxyalkyl, C₂-C₄-cyanoalkyl or, together with R₅₉ and R₆₀ and the nitrogen atom to which they are each attached, R₆₁ forms a pyrrolidine, piperidine, hexamethyleneimine or morpholine ring; An[⊖] is as defined in claim 11; and p is 0 or 1.

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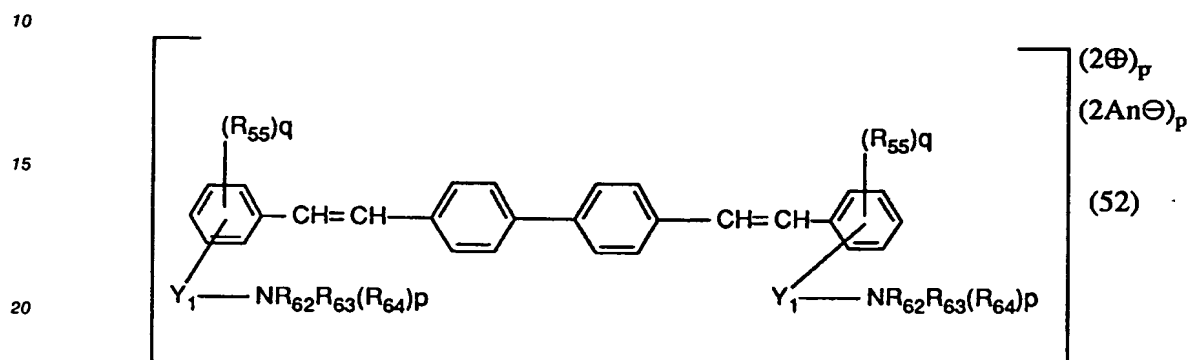
31. A method according to claim 28 in which the cationic bistyrylphenyl fluorescent whitening agent has the formula:

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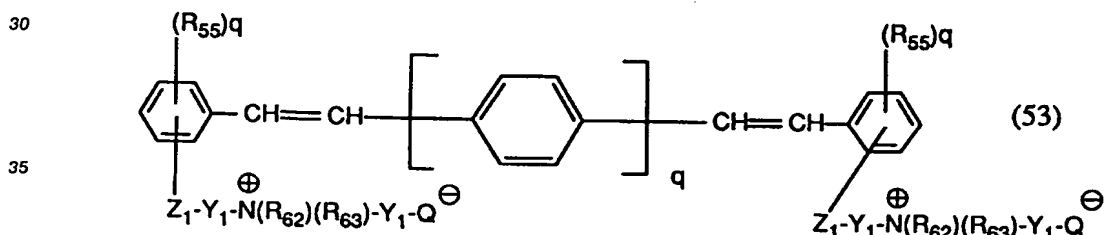
in which R_{55} , Y_1 , $An\Theta$, p and q are as defined in claim 29; R_{62} and R_{63} , independently, are C_1 - C_4 -alkyl or C_2 - C_3 -alkenyl or R_{62} and R_{63} , together with the nitrogen atom to which they are attached, form a pyrrolidine, piperidine, hexamethyleneimine or morpholine ring; R_{64} is hydrogen, C_1 - C_4 -alkyl or C_2 - C_3 -alkenyl or R_{62} , R_{63} and R_{64} , together with the nitrogen atom to which they are attached, form a pyridine or picoline ring; and Z is sulfur, $-SO_2-$, $-SO_2NH-$, $-O-C_1-C_4$ -alkylene- $COO-$ or $-OCO-$.

32. A method according to claim 28 in which the cationic bistyrylphenyl fluorescent whitening agent has the formula:



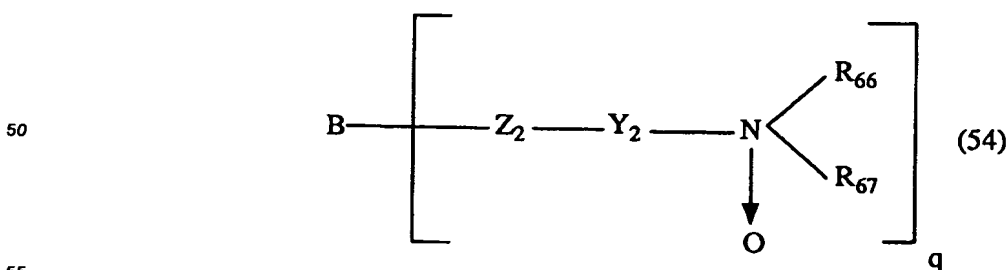
in which R_{55} , R_{62} , R_{63} , R_{64} , Y_1 , $An\Theta$, p and q are as defined in claim 31.

33. A method according to claim 28 in which the amphoteric styrene fluorescent whitening agent has the formula:



in which R_{55} , R_{62} , R_{63} , Y_1 and q are as defined in claim 31 and Z_1 is oxygen, sulfur, a direct bond, $-COO-$, $-CON(R_{65})-$ or $-SO_2N(R_{65})-$ in which R_{65} is hydrogen, C_1 - C_4 -alkyl or cyanoethyl; and Q is $-COO-$ or $-SO_3-$.

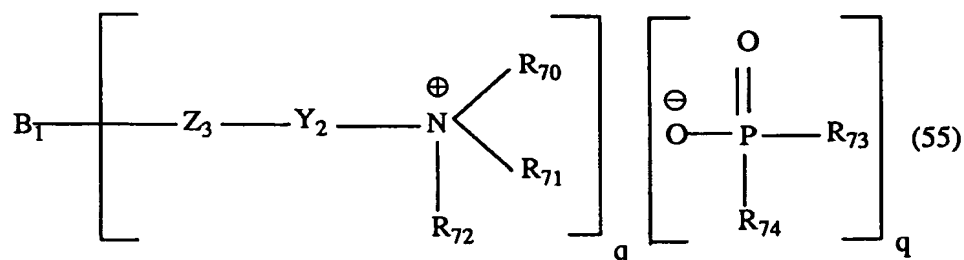
34. A method according to claim 28 in which the amine oxide fluorescent whitening agent has the formula:



in which q is as defined in claim 29; B is a brightener radical selected from a 4,4'-distyrylbiphenyl, 4,4'-divinylstilbene, and a 1,4'-distyrylbenzene, each optionally substituted by one to four substituents

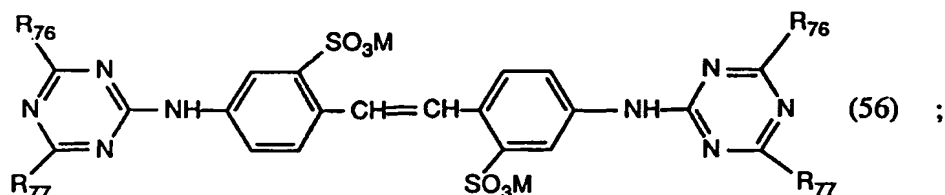
selected from halogen, C₁-C₄-alkyl, C₁-C₄-hydroxyalkyl, C₁-C₄-halogenoalkyl, C₁-C₄-cyanoalkyl, C₁-C₄-alkoxy-C₁-C₄-alkyl, phenyl-C₁-C₄-alkyl, carboxy-C₁-C₄-alkyl, carb-C₁-C₄-alkoxy-C₁-C₄-alkyl, C₁-C₄-alkenyl, C₅-C₈-cycloalkyl, C₁-C₄-alkoxy, C₁-C₄-alkenoxy, C₁-C₄-alkoxycarbonyl, carbamoyl, cyano, C₁-C₄-alkyl-sulfonyl, phenylsulfonyl, C₁-C₄-alkoxysulfonyl, sulfamoyl, hydroxyl, carboxyl, sulfo and trifluoromethyl; Z₂ is a direct bond between B and Y₂, an oxygen atom, a sulfur atom, -SO₂-, -SO₂-O-, -COO-, -CON(R₆₈)- or -SO₂N(R₆₈)- in which R₆₈ is hydrogen or C₁-C₄-alkyl optionally substituted by halogen, cyano, hydroxyl, C₂-C₅-carbalkoxy, C₁-C₄-alkoxy, phenyl, chlorophenyl, methylphenyl, methoxyphenyl, carbamoyl or sulfamoyl; Y₂ is C₂-C₄-alkylene or C₂-C₄-alkyleneoxy-C₂-C₄-alkylene, each optionally substituted by halogen, hydroxyl, C₂-C₅-carbalkoxy, C₁-C₄-alkoxy, phenyl, chlorophenyl, methylphenyl, methoxyphenyl, carbamoyl or sulfamoyl; and R₆₆ and R₆₇, independently, are C₅-C₈-cycloalkyl, C₁-C₄-alkyl or phenyl, each optionally substituted by halogen, hydroxyl, C₂-C₅-carbalkoxy, C₁-C₄-alkoxy, phenyl, chlorophenyl, methylphenyl, methoxyphenyl, carbamoyl or sulfamoyl; in which, in all the carbamoyl or sulfamoyl groups, the nitrogen atom is optionally substituted by one or two C₁-C₄-alkyl, C₁-C₄-hydroxyalkyl, C₂-C₅-cyanoalkyl, C₁-C₄-halogenoalkyl, benzyl or phenyl groups.

35. A method according to claim 28 in which the cationic phosphinic acid salt fluorescent whitening agent has the formula:

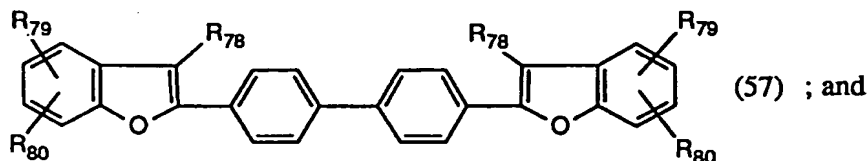


in which q is as defined in claim 29 and Y₂ is as defined in claim 34; B₁ is brightener radical; Z₃ is a direct bond, -SO₂-C₂-C₄-alkyleneoxy, -SO₂-C₂-C₄-alkylene-COO-, -SO₂-, -COO-, -SO₂-C₂-C₄-alkylene-CON(R₇₅)- or -SO₂N(R₇₅)- in which R₇₅ is hydrogen or C₁-C₄-alkyl optionally substituted by hydroxyl, halogen or cyano; R₇₀ is C₁-C₄-alkyl or C₂-C₄-alkenyl, each optionally substituted by halogen, cyano, hydroxy, C₁-C₄-alkoxycarbonyl or C₁-C₄-alkylcarbonyloxy, or R₇₀ is benzyl, optionally substituted by halogen, C₁-C₄-alkyl or C₁-C₄-alkoxy, or R₇₀, together with R₇₁ or Z₃, forms a pyrrolidine, piperidine or morpholine radical; R₇₁ is C₁-C₄-alkyl or C₂-C₄-alkenyl, each optionally substituted by halogen, cyano, hydroxy, C₁-C₄-alkoxycarbonyl or C₁-C₄-alkylcarbonyloxy, or R₇₁ is benzyl, optionally substituted by halogen, C₁-C₄-alkyl or C₁-C₄-alkoxy, or R₇₁, together with R₇₀, forms a pyrrolidine, piperidine or morpholine radical; R₇₂ is C₁-C₄-alkyl; R₇₃ is hydrogen or C₁-C₄-alkyl, optionally substituted by cyano, hydroxy, C₁-C₄-alkoxycarbonyl or C₁-C₄-alkylcarbonyloxy; and R₇₄ is C₁-C₄-alkyl.

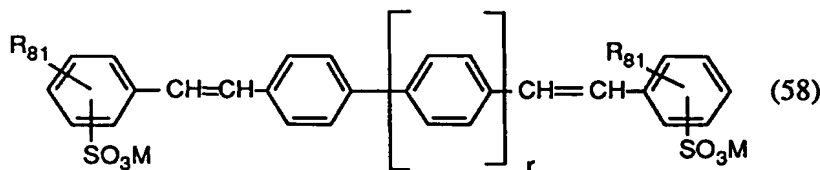
36. A method according to claim 28 in which the bis(triazinyl)diaminostilbene anionic fluorescent whitening agent has the formula:



the dibenzofuranyl biphenyl anionic fluorescent whitening agent has the formula:

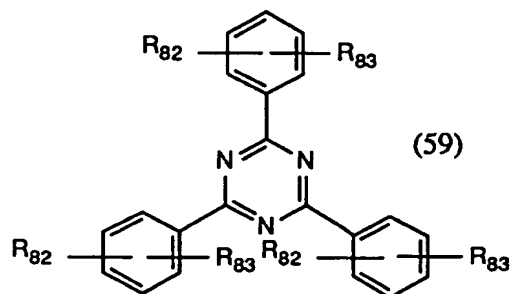


the anionic bistyrylphenyl fluorescent has the formula:

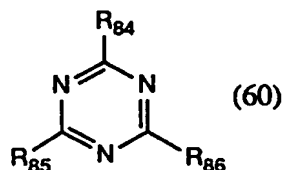


in which R_{76} is phenyl optionally substituted by one or two SO_3M groups and R_{77} is $\text{NH-C}_1\text{-C}_4\text{-alkyl}$, $\text{N(C}_1\text{-C}_4\text{-alkyl)}_2$, $\text{NH-C}_1\text{-C}_4\text{-alkoxy}$, $\text{N(C}_1\text{-C}_4\text{-alkoxy)}_2$, $\text{N(C}_1\text{-C}_4\text{-alkyl)(C}_1\text{-C}_4\text{-hydroxyalkyl)}$, $\text{N(C}_1\text{-C}_4\text{-hydroxyalkyl)}_2$; R_{70} is H, $\text{C}_1\text{-C}_4\text{-alkyl}$, CN, Cl or SO_3M ; R_{79} and R_{80} , independently, are H, $\text{C}_1\text{-C}_4\text{-alkyl}$, SO_3M , CN, Cl or $\text{O-C}_1\text{-C}_4\text{-alkyl}$, provided that at least two of R_{78} , R_{79} and R_{80} are SO_3M and the third group has solubilising character; R_{81} is H, SO_3M , $\text{O-C}_1\text{-C}_4\text{-alkyl}$, CN, Cl, $\text{COO-C}_1\text{-C}_4\text{-alkyl}$, or $\text{CON(C}_1\text{-C}_4\text{-alkyl)}_2$; M is as defined in claim 8; and r is 0 or 1.

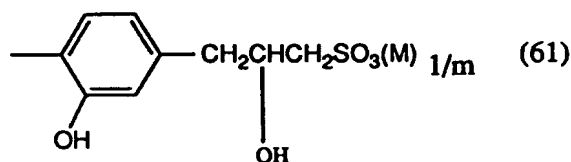
37. A method according to claim 36 in which the compound of formula (56) has the formula (31), (32) or (34), each as defined in claim 26.
38. A method according to claim 36 in which the compound of formula (57) has the formula (43), (44), (45) or (46), each as defined in claim 26.
39. A method according to claim 36 in which the compound of formula (58) has the formula (40), (41) or (42), each as defined in claim 26.
40. A method according to claim 24 in which the fluorescent whitening agent is used together with a UV absorber.
41. A method according to claim 40 in which the UV absorber is an oxalic anilide, an o-hydroxybenzophenone, an o-hydroxyaryl-1,3,5-triazine, a sulphonated-1,3,5-triazine, an o-hydroxyphenylbenzotriazole, a 2-aryl-2H-benzotriazole, a salicylic acid ester, a substituted acrylonitrile, a substituted arylaminoethylene or a nitrilohydrazone.
42. A method according to claim 41 in which the UV absorber is of the benzo-triazine or benzo-triazole class.
43. A method according to claim 42 in which the benzo-triazine UV absorber has the formula:



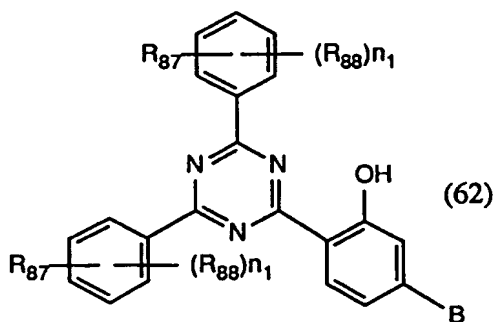
in which R_{82} and R_{83} , independently, are hydrogen, hydroxy or C_1 - C_5 alkoxy; or the formula:



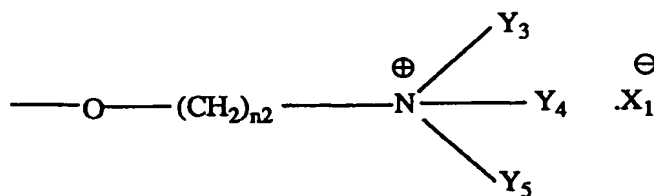
in which at least one of R_{84} , R_{85} and R_{86} is a radical of formula:



in which M is as defined in claim 8; m is 1 or 2; and the remaining substituent(s) R_{84} , R_{85} and R_{86} are, independently, amino, C_1 - C_{12} alkyl, C_1 - C_{12} alkoxy, C_1 - C_{12} alkylthio, mono- or di- C_1 - C_{12} alkylamino, phenyl, phenylthio, anilino or N-phenyl-N- C_1 - C_4 alkylamino, the respective phenyl substituents being optionally substituted by C_1 - C_{12} alkyl or -alkoxy, C_5 - C_8 cycloalkyl or halogen; or the formula:

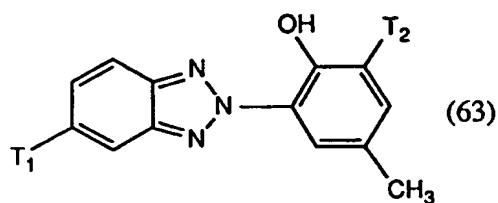


in which R_{87} is hydrogen or hydroxy; R_{88} , independently, are hydrogen or C_1 - C_4 alkyl; n_1 is 1 or 2; and B is a group of formula:

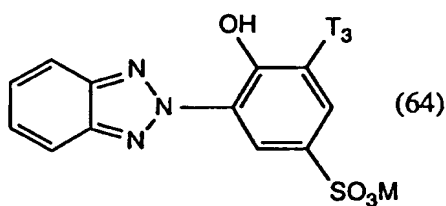


in which n_2 is an integer from 2 to 6; Y_3 and Y_4 , independently, are C_1 - C_4 alkyl optionally substituted by halogen, cyano, hydroxy or C_1 - C_4 alkoxy or Y_3 and Y_4 , together with the nitrogen atom to which they are each attached, form a 5-7 membered heterocyclic ring; Y_5 is hydrogen, C_3 - C_4 alkenyl or C_1 - C_4 alkyl optionally substituted by cyano, hydroxy or C_1 - C_4 alkoxy or Y_3 , Y_4 and Y_5 , together with the nitrogen atom to which they are each attached, form a pyridine or picoline ring; and X_1^{\ominus} is a colourless anion.

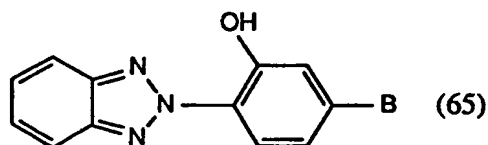
44. A method according to claim 41 in which the triazole UV absorber has the formula:



10 in which T_1 is chlorine or hydrogen; and T_2 is a random statistical mixture of at least three isomeric branched sec. C_8 - C_{30} alkyl groups, each having the formula $-CH(E_1)(E_2)$ in which E_1 is a straight chain C_1 - C_4 alkyl group and E_2 is a straight chain C_4 - C_{15} alkyl group, the total number of carbon atoms in E_1 and E_2 being from 7 to 29; or the formula:



25 in which M is as defined in claim 8; and T_3 is hydrogen, C_1 - C_{12} alkyl or benzyl; or the formula:



in which B is as defined in claim 34.

35 **45.** A method according to claim 44 in which the compound of formula (59) has the formula:

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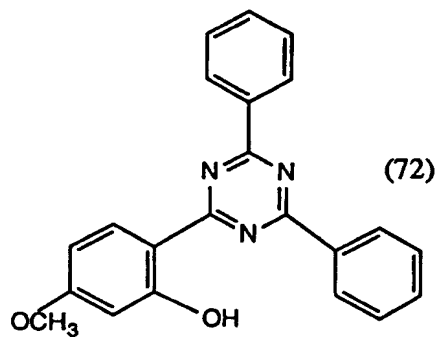
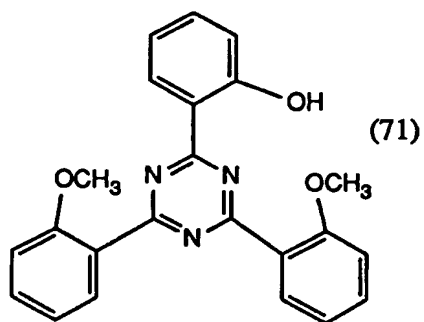
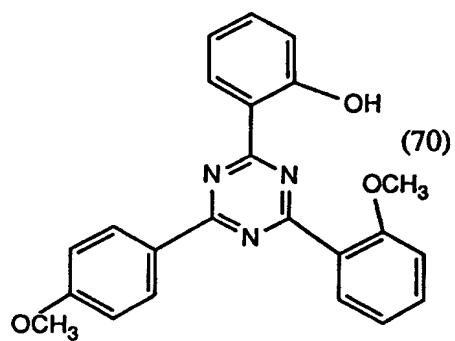
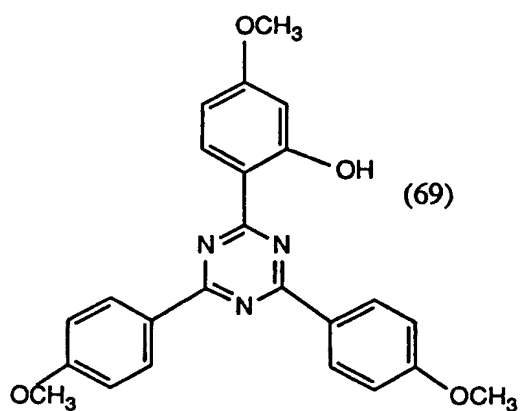
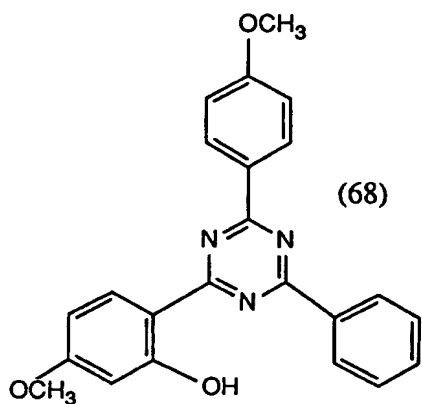
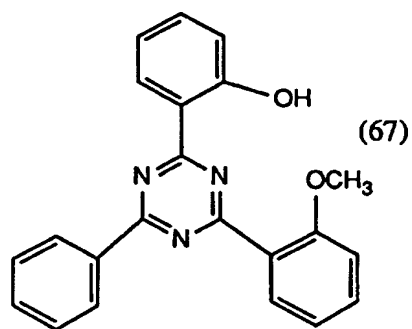
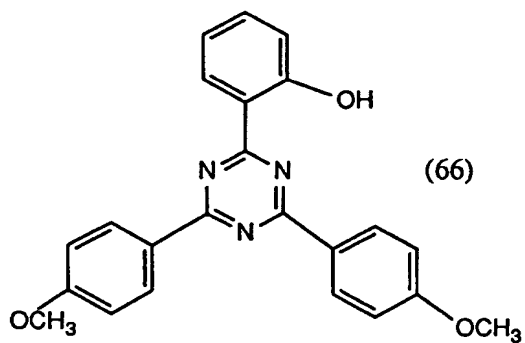
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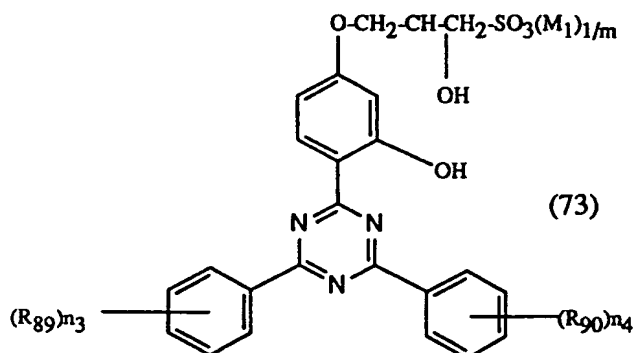
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46. A method according to claim 44 in which the compound of formula (60) has the formula:



in which R_{89} and R_{90} , independently, are C_1 - C_{12} alkyl; m is 1 or 2; M_1 is hydrogen, sodium, potassium, calcium, magnesium, ammonium or tetra- C_1 - C_{12} alkylammonium; and n_3 and n_4 , independently, are 0, 1 or 2.

47. A method according to any of the preceding claims which is conducted in an aqueous medium in which the fluorescent whitening agent is present in solution or as a fine dispersion.

48. A method according to any of claims 4 to 24 and 40 to 47 which is effected from a textile finishing bath and in a neutral, alkaline or acidic bath; or in a solution of the fluorescent whitening agent; or in an emulsion of the fluorescent whitening agent in an organic solvent.

49. A method according to any of claims 4 to 24 and 40 to 48 which is effected from a textile finishing bath and, for the treatment of cotton fabrics, a fluorescent whitening agent of formula (1), (2), (4), (6) or (9) is preferably used; for polyester fabrics, a fluorescent whitening agent of formula (4), (5), (6), (7), (8), (10), (12), (19) or (20) is used; for the treatment of polyamide, a fluorescent whitening agent of formula (1), (2), (4), (5), (6), (7), (8), (10), (11) or (20) is used; for the treatment of polyacrylonitrile, a fluorescent whitening agent of formula (6), (9), (10), (11), (12) or (21) is used; for wool or silk, a fluorescent whitening agent of formula (1), (2), (4), (6), (9), (10) or (11) is used; and for polypropylene, a fluorescent whitening agent of formula (8) is used.

50. A method according to any of claims 4 to 6, 25 and 26 which is effected from a detergent solution by washing the textile fibre material at least once with the detergent composition, at a temperature ranging from 10 to 100 °C.

51. A method according to claim 50 which is effected from a detergent composition comprising:

i) 5-90% of an anionic surfactant and/or a nonionic surfactant;

ii) 5-70% of a builder;

iii) 0-30% of a peroxide;

iv) 0- 10% of a peroxide activator and/or 0- 1% of a bleaching catalyst;

v) 0.005-2% of at least one fluorescent whitening agent which absorbs radiation in the wavelength range 280-400 nm; and

vi) 0.005-10% of one or more auxiliaries, each by weight, based on the total weight of the detergent.

52. A method according to any of claims 4 to 6, 25, 26, 50 and 51 which is effected from a detergent composition and, for the treatment of polyester fabrics a fluorescent whitening agent of formula (28) is used; for the treatment of polyamide, a fluorescent whitening agent of formula (29), (30) or (34) is used; and for wool, a fluorescent whitening agent of formula (29), (30) or (37) is used.

53. A stable, concentrated fabric care composition comprising 0.3 to 10% by weight of a fluorescent whitening agent which is compatible with a fabric care ingredient, based on the total weight of the composition, and a fabric care ingredient, the remainder being substantially water.

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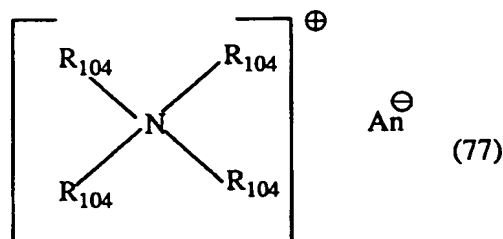


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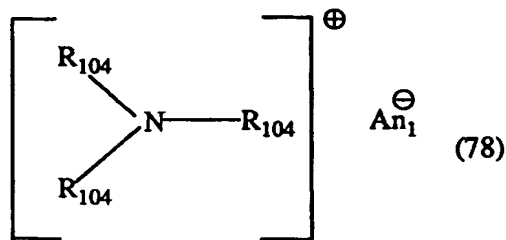


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in which An^{\ominus} is as defined in claim 11 and the groups R_{104} may be the same or different and each is a C_1 - C_{30} aliphatic residue, C_1 - C_4 hydroxyalkyl, $C_2H_4OC(=O)R_{92}$, $C_2H_4NHC(=O)R_{92}$ or $CH_2CH[OC(=O)R_{92}][CH_2OC(=O)R_{92}]$, in which R_{92} is as defined in claim 56, provided that at least one group R_{104} is C_{14} - C_{30} alkyl, $C_2H_4OC(=O)C_{14}$ - C_{30} alkyl, $C_2H_4NHC(=O)C_{14}$ - C_{30} alkyl or $CH_2CH[OC(=O)C_{14}$ - C_{30} alkyl][$CH_2OC(=O)C_{14}$ - C_{30} alkyl].

58. A composition according to claim 55 in which the ester amide amine cationic fabric softening agent has the formula:



in which R_{104} is as defined in claim 57 and An_1^{\ominus} is an inorganic or organic acid from which an anion An^{\ominus} is derived, wherein An^{\ominus} has its previous significance, provided that at least one group R_{104} is C_{14} - C_{30} alkyl, $(CH_2)_nOC(=O)C_{14}$ - C_{30} alkyl, $(CH_2)_{n_2}NHC(=O)C_{14}$ - C_{30} alkyl or $CH_2CH[OC(=O)C_{14}$ - C_{30} alkyl][$CH_2OC(=O)C_{14}$ - C_{30} alkyl], in which n_2 is as defined in claim 43.

59. A method for the treatment of a textile article, comprising applying, to a previously washed article, a fabric rinse composition comprising 0.3 to 10% by weight of a cationic, amphoteric or anionic fluorescent whitening agent, based on the total weight of the composition, and optionally a fabric care ingredient, the remainder being substantially water.

60. A method according to claim 59 which comprises applying, to the previously washed article, a rinse cycle fabric softener composition comprising 5 to 25 % by weight of a cationic fabric softening agent and 0.3 to 10 % by weight of a cationic, amphoteric or anionic fluorescent whitening agent, each based on the total weight of the composition, the remainder being substantially water.